

September 2015

# Science & Technology

REVIEW

## **COMPUTATIONALLY TAKING ON GRAND CHALLENGES**

*Also in this issue:*

**Engineering Tougher Biofuel Bacteria**

**Supercapacitors Reveal Their Secrets**

**Overturning a Long-Used Equation**

## About the Cover

Now in its tenth year, Livermore's Computing Grand Challenge Program has already left a substantial legacy of significant achievements in cutting-edge research important to the nation. Each year, the program provides competitively selected projects with access to world-class computing resources. As the article beginning on p. 4 describes, mission-relevant research funded by the program includes laser ignition experiment modeling, first-principles molecular dynamics (MD) simulations, and climate modeling. The artist's imagery on the cover represents program-funded MD research into the behavior of hydrogen at extreme environments, such as those found on Saturn and Jupiter, where the molecular solid can transition to a quantum liquid.



Cover design: Kitty Madison

## About S&TR

At Lawrence Livermore National Laboratory, we focus on science and technology research to ensure our nation's security. We also apply that expertise to solve other important national problems in energy, bioscience, and the environment. *Science & Technology Review* is published eight times a year to communicate, to a broad audience, the Laboratory's scientific and technological accomplishments in fulfilling its primary missions. The publication's goal is to help readers understand these accomplishments and appreciate their value to the individual citizen, the nation, and the world.

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## NuSTAR Examines Supernova Asymmetry

New results from NASA's Nuclear Spectroscopic Telescope Array (NuSTAR) show that a supernova close to our galaxy experienced a single-sided explosion, providing compelling observational evidence that supernovae are not symmetric. A team of scientists including Livermore's Michael Pivovarov, Julia Vogel, Todd Decker, and Nicolai Brejnholt studied x-ray emissions taken with NuSTAR and found that the Supernova 1987A explosion was highly asymmetric. The results appeared in the May 8, 2015, edition of the high-profile journal *Science*.

Supernova 1987A is a supernova remnant that evolved from a core-collapse supernova. This type of explosion produces an isotope of titanium in its innermost ejecta, the layer of material directly above the newly formed remnant. The radioactive decay of this isotope provides a direct probe of the supernova engine. NuSTAR measurements confirm that heavy elements are moving at speeds several times faster than expected from spherically symmetric models. The image of Supernova 1987A—courtesy of the ALMA Observatory, A. Angelich, the Hubble Space Telescope, and Chandra X-Ray Observatory—shows newly formed dust in the center (red) and the expanding shock wave colliding with a ring of material (green and blue).

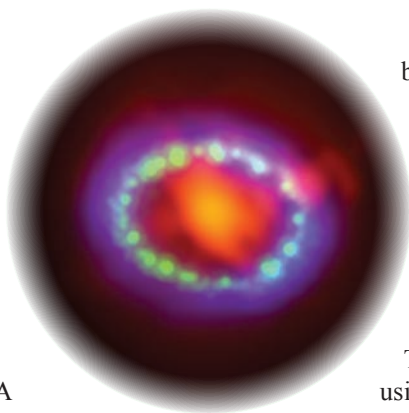
NuSTAR, a NASA *Explorer*-class mission launched in June 2012, is designed to detect the highest energy x-ray light in great detail. NuSTAR uses technology developed by Livermore for the Laboratory's High Energy Focusing Telescope (HEFT). The x-ray-focusing abilities, optics principles, and fabrication approach of NuSTAR are based on those developed under the HEFT project. Pivovarov and Vogel are part of the team that received a NASA award in September 2014 "for exceptional achievement in executing the NuSTAR science program leading to groundbreaking discoveries in high-energy astrophysics."

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## One Step Closer to Mimicking Gamma-ray Bursts

Using high-energy lasers, Laboratory researchers have produced a record number of electron-positron pairs, opening opportunities to study extreme astrophysical processes such as black-hole formation and gamma-ray bursts. In May of this year, Livermore physicist Hui Chen and her colleagues created nearly a trillion positrons, as compared to billions of positrons in previous experiments.

Positrons are antimatter particles having the same mass as an electron but the opposite charge. The generation of energetic electron-positron pairs is common in extreme astrophysical environments associated with the rapid collapse of stars and the formation of black holes. These pairs radiate their energy, producing extremely



bright gamma-ray bursts, which are the brightest electromagnetic events known to occur in the universe, but the mechanism of how they are produced is still a mystery.

Electron-positron pairs are generated in the lab by shining intense laser light into a gold foil. This produces high-energy radiation, creating electron-positron pairs as the laser interacts with the nucleus of the gold atoms.

The ability to create a large number of positrons using energetic lasers opens the door to several new avenues of antimatter research. Antimatter research

could reveal why more matter than antimatter survived the Big Bang at the start of the universe, why the observable universe is apparently almost entirely matter, whether other places are almost entirely antimatter, and what might be possible if antimatter could be harnessed.

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## Livermore Helps Advance Ebola Test

Researchers from Lawrence Livermore have assisted San Francisco Bay Area biomedical company Cepheid in advancing its Ebola virus detection test for use. The Livermore testing was performed by Reg Beer, Livermore's medical diagnostics initiative program leader, and biomedical scientists Pejman Naraghi-Arani and Celena Carrillo. Cepheid, co-founded in 1996 by former Livermore researcher M. Allen Northrup, is a molecular diagnostics company that works to improve health care by developing, manufacturing, and marketing accurate and easy-to-use molecular systems and tests.

Laboratory researchers received a Cepheid GeneXpert system and experimental Ebola assay cartridges, testing them against non-Ebola bacterial and viral targets to demonstrate that the assay would only detect Ebola. "This exclusivity testing supported Cepheid's successful request to the FDA for an emergency-use authorization with the current Ebola outbreak," says Beer. Livermore scientists tested 25 target organisms, including inactivated RNA from multiple strains of Ebola virus and Marburg virus.

In addition to providing valuable accuracy and other data to the company, Livermore was also one of the first sites outside of Cepheid to use the assay, providing feedback on usability and user interface issues. The Laboratory's collaboration with Cepheid is expected to continue as Livermore researchers provide the firm with an accurate quantification of viral RNA samples that would be used for testing. On May 13, 2015, Cepheid also announced that the World Health Organization had listed Cepheid's Ebola test, which can deliver results in less than two hours, as eligible for procurement for Ebola-affected nations.

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# Empowering Research in Mission-Relevant Basic Science

**T**HE Department of Energy's Accelerated Strategic Computing Initiative—now the Advanced Simulation and Computing (ASC) Program—has secured an enduring position in Lawrence Livermore's computing legacy through its advancement of high-performance computing (HPC) hardware, software, and application development in support of science-based stockpile stewardship. The complementary unclassified Multiprogrammatic and Institutional Computing (M&IC) Program, developed by Livermore soon after, helped ensure HPC was available to all Livermore scientists, enhancing the vitality of the institution's science and technology and helping retain a top-tier scientific workforce.

Today, nearly two decades after it started, M&IC allocates time on unclassified systems through three channels: the Laboratory Directed Research and Development Program, the discovery-focused Computing Grand Challenge Program, and strategic capability banks. The Computing Grand Challenge Program, whose projects consume the largest portion of M&IC resources, was launched in 2005 to provide unclassified capability computing that would allow researchers to exploit the significant advantages of working at scale. As discussed in the article beginning on p. 4, the Computing Grand Challenge Program grants scientists with big ideas the computing resources they need to tackle otherwise insurmountable mission-relevant scientific challenges.

Classified and unclassified computing have a synergistic relationship. Advances in algorithm development or modeling made through Grand Challenges and other unclassified research initiatives often benefit classified research efforts, while supercomputing infrastructure and expertise developed for classified research enhances unclassified resources. For instance, Vulcan, the most powerful system available to Grand Challenge winners, is a smaller version of Livermore's leading ASC machine, Sequoia, the world's third most powerful supercomputer, which Livermore computer scientists helped design.

Livermore's world-class HPC ecosystem—its hardware, software, and computer support staff—empowers scientific discovery and technology development on both the classified and unclassified fronts in support of our institution's vital missions for the nation. Maintaining the necessary competitive edge in the rapidly evolving world of HPC requires that we work on three timescales simultaneously: delivering capabilities today, innovating for and investing in tomorrow, and envisioning

what will come the day after tomorrow, that is, what is next on the horizon.

We are currently addressing the “tomorrow” trajectory in several exciting ways. One is by modernizing our computing infrastructure. In May, the Laboratory broke ground on a modular and sustainable supercomputing facility to help meet the growing need for unclassified computing at Livermore and to accommodate a variety of HPC architectures. Another is by preparing existing and new applications to run on Sierra, Livermore's next ASC advanced technology system. Sierra is part of the Collaboration of Oak Ridge, Argonne, and Livermore (CORAL). A procurement collaboration between the three national laboratories and industry partners, CORAL seeks to develop and deliver next-generation petaflop-scale ( $10^{15}$  floating-point operations per second) systems to the three laboratories in 2017 or 2018. As with Sequoia, Sierra will be made available for marquee unclassified calculations before it enters into classified operations, to identify and resolve any security and stability issues while supporting scientific discovery.

The “day after tomorrow” scenario is computing at the exascale—speeds of  $10^{18}$  flops and memory of  $10^{18}$  bytes. Our computer scientists have long been planning and preparing for extreme-scale computing, but a new multi-agency government initiative is bringing it one step closer to realization. In July, President Obama established the National Strategic Computing Initiative, which aims to create, before 2025, the world's first exascale computer. This machine will be more than 30 times faster than today's fastest systems. Livermore and other national laboratories will play a key role in the design and development of this new class of computers. Such initiatives will help keep the United States at the forefront of HPC capabilities and enable institutions such as Livermore to continue pushing scientific and computational boundaries.

Modern scientific advances rely on a robust and dynamic computing ecosystem, which Lawrence Livermore maintains through programs such as ASC and M&IC. Strategically deploying these resources through the Computing Grand Challenge Program and other efforts supports our national security missions and gives researchers some of the tools they need to take on big scientific and engineering challenges.

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■ Dona Crawford is associate director for Computation.

# SCIENCE on a GRAND SCALE

*Through the Computing Grand Challenge Program, participants harness world-leading supercomputing and science to advance scientific discovery and Laboratory missions.*

**S**INCE its inception in 2005, Lawrence Livermore's Computing Grand Challenge Program has awarded unclassified computing time on flagship institutional computing resources to scientists and engineers pursuing ambitious but achievable goals that advance national security or basic science research. (See *S&TR*, July/August 2011, pp. 13–19.) Now entering its second decade, the program is cultivating ideas and advances that are as important as ever. Fred Streitz, director of Livermore's High-Performance Computing Innovation Center and co-lead for the Grand Challenge Program, notes, "Grand Challenges are about encouraging people to think larger and giving them a venue to push the limits, scientifically and computationally."

These efforts have been aided by the ongoing evolution of high-performance computing (HPC). Clock speeds and numbers of processors have continued to climb, as exemplified by the changes in Grand Challenge resources, from the 20-teraflop (a teraflop equals  $10^{12}$  floating-point operations per second), 4,000-processor Thunder supercomputer



Computational scientist Erik Draeger stands in front of a large, multiple-projector display of research simulating atomic-level behavior at the anode–electrolyte interface of a lithium-ion cell. Performed on Livermore’s Vulcan supercomputer, this simulation exemplifies the sort of cutting-edge research that is supported by the Computing Grand Challenge Program. (Photograph by George A. Kitrinos.)

used by Grand Challenge researchers in 2005 to the 5-petaflop ( $10^{15}$  flops), 400,000-processor Vulcan system available today. Architectures have also undergone more subtle changes, such as graphics processing units, in-processor memory, and custom central processing units. These trends have expanded the size and complexity of systems that can be modeled effectively. Innovations in computer architecture at Livermore have also expanded the scope of accessible research. For instance, this year's competition welcomed, for the first time, proposals for the 150-teraflop Catalyst supercomputer, which is especially designed to solve big-data analytics problems. "Catalyst is a different type of machine and allows Grand Challenges in a very different space than the others," says Streitz.

Although the computing resources are the enabler, the success of projects relies on the strength of the researchers' ideas. The program aims to inspire researchers not simply to scale up an existing solution, but to enhance or even reframe their investigations. Computer scientist Erik Draeger, a member of the Grand Challenge project selection committee, says, "The point of the program is to get scientists thinking in new directions. We have this

great hardware, but we're not making the most of it if we continue to think about problems in the same old way." Grand Challenge projects span many fields of research, including target simulations for the National Ignition Facility (NIF), which aid fusion energy science and stockpile stewardship research; first-principles molecular dynamics (MD) simulations, which support a wide range of basic and applied science efforts; and climate modeling, which has national and global security applications.

### When Laser Meets Plasma

During fusion ignition experiments at NIF, multiple laser beams simultaneously enter through holes in a tiny metal container known as a hohlraum, striking the inside walls and producing x rays that compress the capsule of frozen fusion fuel in the hohlraum. To achieve the extreme temperatures and pressures such experiments require, laser light must be delivered to and absorbed by the hohlraum walls with great precision. Unfortunately, hohlraum conditions also invariably generate plasma, a gas of charged particles that can interfere with the experiment by misdirecting laser energy. Bent or scattered light can lower the temperature in the hohlraum and interfere

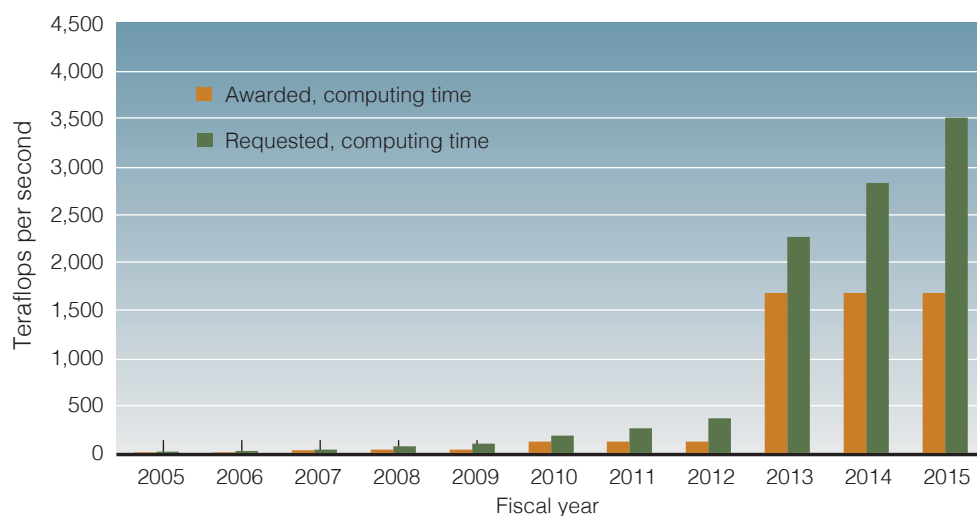
with symmetrical fuel compression and even cause facility damage if reflected back at the laser optics. (See *S&TR*, June 2010, pp. 17–19.)

The quest to understand, predict, and mitigate laser–plasma interactions (LPI) in NIF targets began 21 years ago, when NIF was little more than a collection of blueprints and plans, with the development of the three-dimensional (3D) LPI modeling code F3D, now called pF3D. Accurately simulating LPI is difficult and computationally intensive, as laser energy and plasma interact in complex, highly nonlinear ways. (See *S&TR*, January/February 2009, pp. 11–15; and January/February 2005, pp. 4–13.) The relevant phenomena span extremes in length and time, from macro to micro. Bridging these extremes is the computationally most challenging physics component—the mesoscale, the micrometer and picosecond scale behavior that pF3D seeks to understand.

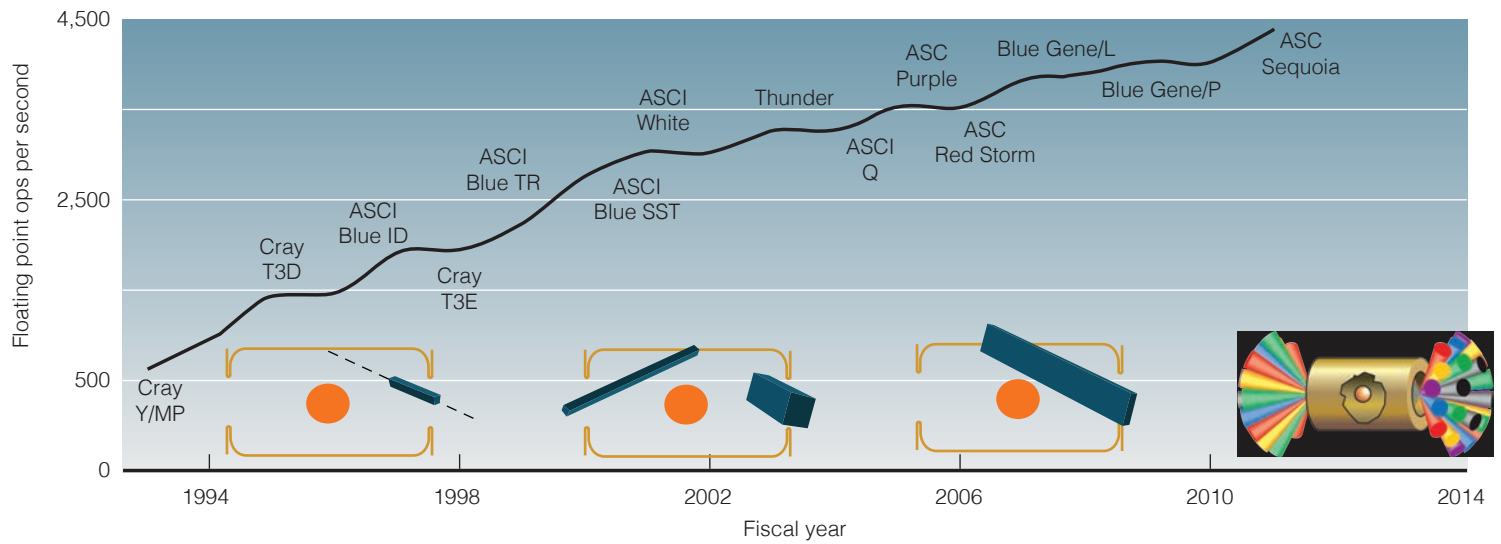
Over the past two decades, LPI modeling has benefited from rapidly increasing computer performance at Lawrence Livermore. Bert Still, who served as pF3D's principal developer for many years, recalls a calculation he performed for NIF's groundbreaking ceremony in 1995: "The initial calculation was 128 by 128 by 512 cells and took an entire supercomputer to run. It only included forward light propagation and was pretty primitive by modern standards. Now I could do that calculation with the computing power in my cellular phone." At the time, researchers could only model a single thin beam filament near the entrance of the hohlraum interacting with homogeneous plasma.

### Atlas Raises the Bar

LPI modeling efforts intensified in 2005, when a key external review of NIF technological readiness emphasized the need for 3D LPI simulations that could help evaluate potential ignition target designs. NIF was still under construction, and the laser power anticipated for ignition experiments was unprecedented. Pinpointing the target design and



Livermore's Computing Grand Challenge Program has seen growth in both requested and available time over its 10-year history, but demand has always exceeded supply.



The growth in computer performance at Livermore has enabled researchers to improve their laser-plasma interaction modeling capabilities. In 2009, for instance, researchers using an enhanced version of the code pF3D could perform calculations a million times larger—and therefore far more realistic—than those done in 1995 with an earlier version of the same code. The hohlraum illustrations on the bottom represent how greater supercomputing power has enabled increased complexity in simulations of National Ignition Facility (NIF) experiments.

experimental conditions most likely to meet the physics requirements while avoiding optics damage was imperative. Radiation hydrodynamics modeling expert Debbie Callahan observes, “We were dealing with a new machine, more energy, and a bigger plasma, all of which made prediction tough.” That year, using the Thunder supercomputer, the researchers were able to model the full two-millimeter-diameter laser beam, though still only for a short distance at the hohlraum entrance. Importantly, they simulated for the first time the large gradients in the plasma caused by temperature, electron density, and ion density variations that can affect the type and amount of light scatter that occurs.

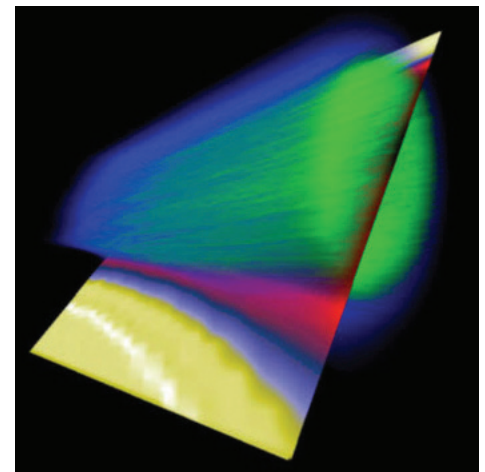
In 2007 and 2008, Livermore LPI researchers received Grand Challenge awards totaling 16 million hours of machine time on the 44-teraflop Atlas supercomputer, enabling the team to take LPI simulation to a new level, both in size and amount of incorporated physics. Even with Atlas, the researchers could not simulate the whole beam, so they analyzed millimeter-scale radiation-hydrodynamics

simulations to determine when and where LPI was most likely to occur. Using the parameters set by these models and information gained from electron-scale modeling, they performed pF3D simulations of relevant spans of the laser beam’s path from the hohlraum entrance to its inner wall. Results were then fed back into the radiation-hydrodynamics model to help converge on a safe and optimized target design. These pF3D simulations provided motivation to lower the radiation temperature in the hohlraum, thereby reducing LPI effects, for instance. The most significant outcome of the Grand Challenge, however, was a modeling methodology for LPI prediction and target design evaluation that would prove vital as NIF experiments began in 2009.

LPI modeling expert Denise Hinkel says, “The Atlas simulations positioned us to be in the best space we could be when we turned on NIF. We were able to quickly address questions that arose.” They also laid the foundation for 2009 runs on the 500-teraflop Dawn supercomputer in which the researchers first simulated a full beam travelling the entire distance between the

hohlraum’s entrance and wall for roughly 100 picoseconds.

LPI modeling continues to shed light on phenomena not easily understood through experiments alone. The knowledge gained



The first-ever whole-beam pF3D simulation for a NIF ignition target was performed in 2009 on the Dawn supercomputer. Such simulations have helped ensure that target designs minimize misdirected light, which can impede the experiment and even damage the optics.

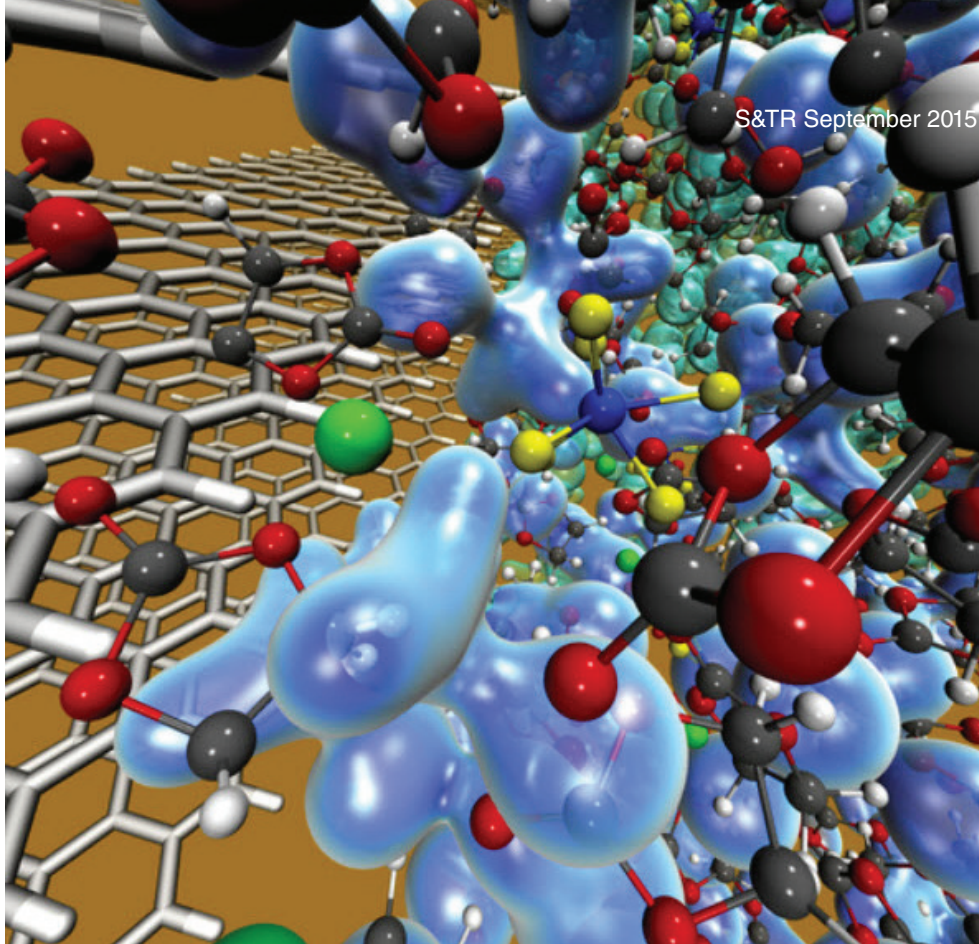
from simulations has, for instance, prompted NIF researchers to purposefully generate an LPI effect called crossbeam transfer and use it to achieve a more symmetrical implosion—a novel and effective approach. (See *S&TR*, March 2013, pp. 10–17.) According to Hinkel, the next true grand challenges in NIF modeling will be modeling LPI for multiple beams and integrating the three temporal and spatial scales of simulation, which will require computing at the exaflop ( $10^{18}$  flops) scale. The equivalent of 36 Dawns, for example, will be needed to model the interactions between plasma and several laser beams.

### Take It from the Top

Standard MD simulations use empirical data in their calculations. (See *S&TR*, January/February 2006, pp. 11–17.) However, for complex systems or those under extreme conditions, gathering enough reliable experimental results to constrain all of the MD simulation's parameters can be difficult. An alternative approach for researchers is to bypass models and experiments and calculate the properties of materials from first principles—that is, directly from physics equations.

The Schrödinger equation, a multidimensional differential equation, can be used to understand the behavior of atoms and electrons at a quantum level, but solving the equation directly is computationally intractable for all but the smallest and simplest molecules, even on today's supercomputers. Instead, scientists rely on physical and numerical approximations for computing electronic structure, with the accuracy of these calculations depending on the approximations chosen. Even with approximations, the computational cost for first-principles MD is high, limiting the size and scope of what can be studied.

For instance, a decade ago, billion-atom classical MD calculations were common, while routine first-principle runs were restricted to just 50 atoms. Draeger notes, “A couple of hundred atoms was a huge challenge then. Now, with Grand Challenge



An image from a 25-picosecond, 1,700-atom Qbox simulation performed on the Vulcan supercomputer shows a lithium-ion cell anode–electrolyte interface. Qbox is a first-principles molecular dynamics (MD) code written to efficiently carry out large simulations on massively parallel supercomputers, allowing researchers to study systems with larger numbers of atoms than is possible with most other codes of its type.

resources, we can study thousands of atoms. Complexity in first-principles simulations goes up cubically, not linearly, so today we're solving problems that are thousands of times more difficult, on millions of times the resources.” The growth in HPC capabilities has enabled researchers to employ better approximations, study bigger problems, and explore new classes of chemical systems, including heterogeneous molecular interactions and extreme behavior such as shocks.

One of the codes that has allowed Livermore researchers to make strides in first-principles modeling is Qbox, an open-source application for which Draeger is lead Livermore developer. (See *S&TR*, November 2006, pp. 4–11.) Qbox uses the density functional theory (DFT) approximation approach, prized for its favorable ratio between precision

and computational cost. Most popular DFT codes were developed by and for academic researchers who only had access to hundreds or thousands of cores and so tend to run inefficiently on Livermore's massively parallel computing systems. Qbox, however, was designed for and thrives on such systems, allowing researchers to study larger numbers of atoms than is possible with most other DFT codes. Notes Draeger, “Qbox is a good example of how Grand Challenge support affects code design. It's a top-down rather than a bottom-up design.”

### Putting Pressure on Hydrogen

Although DFT has proved a valuable and economical approach to first-principles MD simulations, some situations call for the greater accuracy permitted by quantum Monte Carlo (QMC). Unfortunately, QMC

is far more computationally expensive. (See *S&TR*, May 2007, pp. 4–11.) With support from the Grand Challenge and the Laboratory Directed Research and Development Programs, researcher Miguel Morales and his collaborators at the University of L'Aquila in Italy and the University of Illinois at Urbana-Champaign have been developing a more predictive first-principles approach that combines QMC and DFT. Their effort focuses on the behavior of hydrogen at extreme conditions—millions of degrees kelvin and millions of atmospheres. (See *S&TR*, January 2015, pp. 23–26.)

“We chose hydrogen due to its high impact and because it’s a simple enough element that we can bring all of the techniques we’ve developed over the last decade to bear, in terms of describing properties from computer simulation without experimental input. It’s still a very ambitious project that requires the largest computer resources we can get,” says Morales. Thanks to the Grand Challenge Program, those resources have included the 260-teraflop Sierra and 5-petaflop Vulcan systems. The project not only refines an important predictive computational method but also aims to shed light on planetary formation. Gas giants, such as Jupiter, are over 90 percent hydrogen and helium, and pressures and temperatures within the planets can vary by orders of magnitude, necessitating an accurate phase diagram covering a large range of thermodynamic conditions.

Technological limitations have also restricted the experimental data available for high-pressure hydrogen, a regime where DFT first-principles methods have struggled quantitatively. “To correctly model the interior of Jupiter, we need to know when and how certain transitions happen,” explains Morales, “but that is precisely where DFT becomes inaccurate.” Morales’ solution has been to use a combination of methods. QMC is used to check the accuracy of DFT calculations, particularly around key transitions, such as when dense liquid

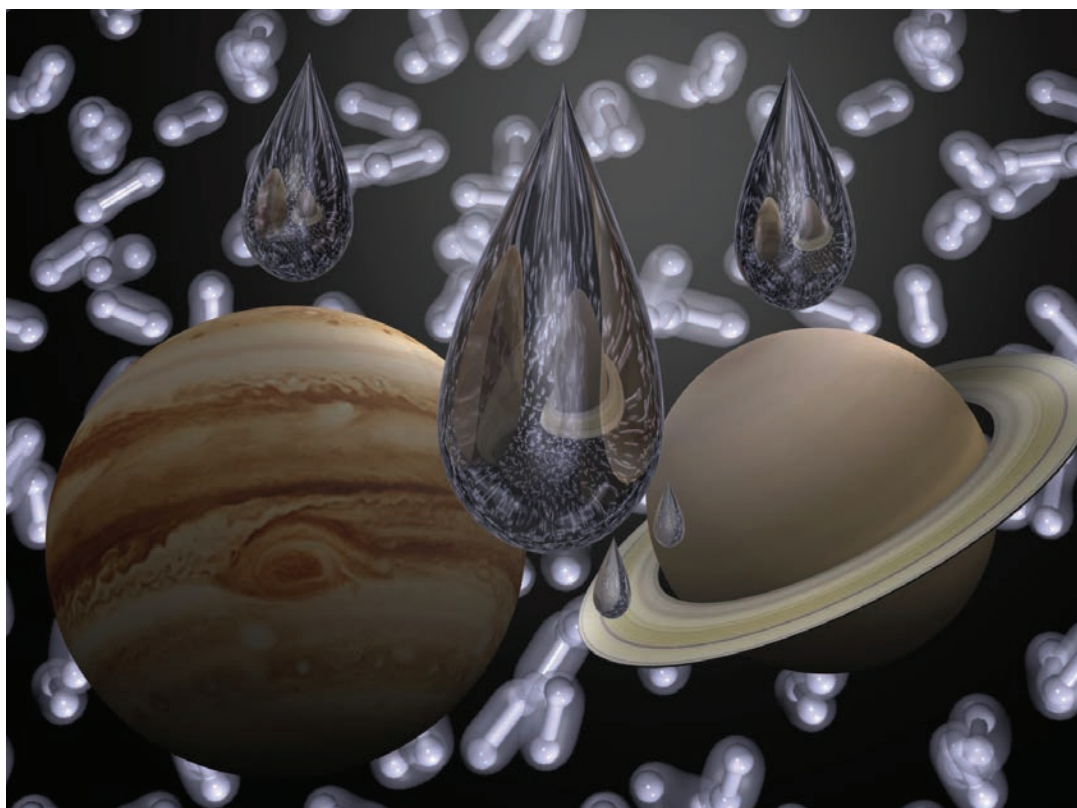
hydrogen changes from metal to insulator. “The more expensive method acts as the decision-making guide for the less expensive one,” he adds.

This approach is enabling scientists to more precisely pinpoint when and how phase transitions occur, including the metallization of solid hydrogen, a high-temperature superconductor candidate. “At this point,” says Morales, “we have results that match very well with our experimental data. Such data only exists in small slivers, so we benchmark our methods on the experiments and then go and explore areas that haven’t been explored in experiments.” While Morales has been successfully demonstrating a hybrid approach to first-principles MD

simulations, other Livermore researchers have begun examining how to reduce the resource intensiveness of the calculations themselves—an ambitious effort. “The next major effort at Livermore will be to create new algorithms that knock the complexity down from  $n^3$  to  $n$ , like classic MD,” says Draeger.

### New Heights in Climate Modeling

Climate modeling has benefited greatly from the steep climb in computing capability over the past several decades. In 1998, a 1-year simulation of global climate using 300-kilometer resolution could be run in a day on a supercomputer. The same model can now be run on a high-end



Livermore researchers are using a combination of first-principles MD approaches to better understand the phase diagram of hydrogen, particularly at high pressure, where it exhibits transitions such as from a molecular solid to a quantum liquid, as this artist’s rendering suggests. This research will likely shed light on the formation of planets such as Jupiter and Saturn, which are mostly composed of hydrogen and helium.

desktop machine in minutes. Climate scientists have responded by creating more detailed and accurate simulations, using finer resolutions, more variables, and longer time spans. The additional computing horsepower is also allowing them to refine methods for characterizing and reducing uncertainty, giving them greater confidence in their modeling projections. At Livermore, a series of Grand Challenge efforts has accelerated the development of these higher performance models and uncertainty quantification methods, with which climate researchers can gain new insights into Earth's climatic past, present, and future.

The first of these Grand Challenge projects, performed from 2005 to 2007 on the Thunder supercomputer, evaluated a computationally intensive approach for improving regional climate prediction called dynamical downscaling. This approach uses high-resolution simulations of global climate to drive even higher resolution regional-scale models. Govindasamy Bala's team employed the primary U.S. general circulation model, known as the Community Climate System Model (CCSM), to perform a 400-year global simulation with improved results for global surface winds and sea surface temperatures. At 100-kilometer resolution, this was the highest resolution multicentury CCSM simulation performed to date.

Results of the global simulation served as initial conditions and boundary data for

12-kilometer-scale calculations of climate change in California over four decades using the Weather and Research Forecasting model. Both the resolution and duration of the regional simulations were unparalleled in regional climate modeling. The resolution enabled the team to resolve more of California's complex topography, such as details in mountainous areas, and the length of the run allowed for a better sampling of natural variability, increasing the credibility of model predictions. Comparison with observational datasets and global modeling data confirmed that dynamical downscaling provides valuable insights into regional climate behavior, such as small-scale atmospheric features that cannot readily be captured in a global model.

### Climate Clarity through Uncertainty

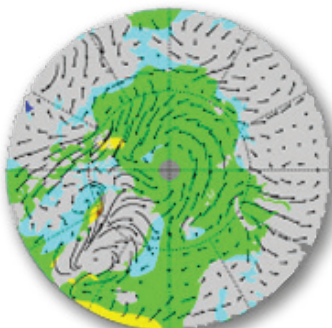
CCSM also featured heavily in a 2008 Grand Challenge effort led by Dave Bader. Using 8 million hours of Atlas processor time to complete a simulation of the global climate under present-day conditions—a necessary precursor to climate projection—the team achieved what Bader describes as “an unprecedented realism of phenomena.” The 20-year simulation was configured using grid resolutions of 11 kilometers for the ocean and sea ice and 28 kilometers for the atmosphere and land. This was the first study with fine enough oceanic and atmospheric horizontal resolution to simulate turbulent instabilities in the large-scale circulation—for instance, the

formation and propagation of tropical cyclones, the frequency and intensity of which many researchers project will be affected by climate change. The major outcome of the project, though, was a process for performing ultrahigh-resolution global climate modeling. “Ten years ago, the big challenge was weather-scale climate modeling,” says Bader. “The Grand Challenge project put us on the path to doing this kind of modeling routinely.”

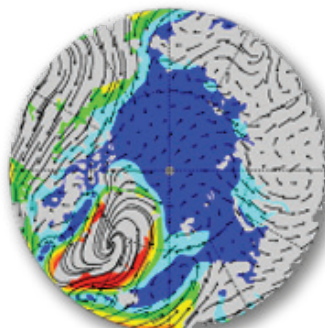
A third Grand Challenge, led by Richard Klein from 2009 to 2011, applied rigorous and computationally demanding uncertainty quantification methods developed for the Stockpile Stewardship Program to climate prediction. (See *S&TR*, July/August 2010, pp. 12–14.) Uncertainty can take many forms. Simply using climate models to assess climate change introduces uncertainty because the models do not perfectly represent the climate system, and the various models respond differently to the same input. In fact, more than 100 parameters, each with associated uncertainties, can influence climate simulation predictions. Uncertainty quantification is performed with an ensemble of models. Klein's team is running CCSM on Atlas and Sierra—along with an intelligent, self-adapting search tool they developed—to generate a comprehensive set of climate simulations and comb through possible combinations of input parameters. This methodology is enabling researchers to pinpoint, measure, and potentially reduce

The plot shows modeled (middle and right) and observed (left) surface wind circulation in the summertime in the Arctic. Using finite-volume transport, an improved method for simulating global surface winds and sea surface temperatures, Livermore global climate simulations were able to better simulate features such as cyclonic circulation than with traditional modeling methods.

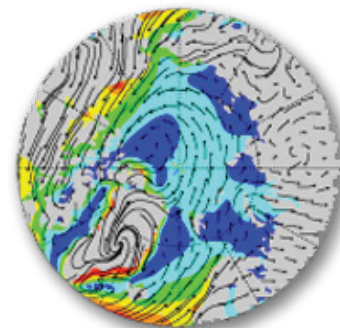
Analysis of observed data



Spectral simulation



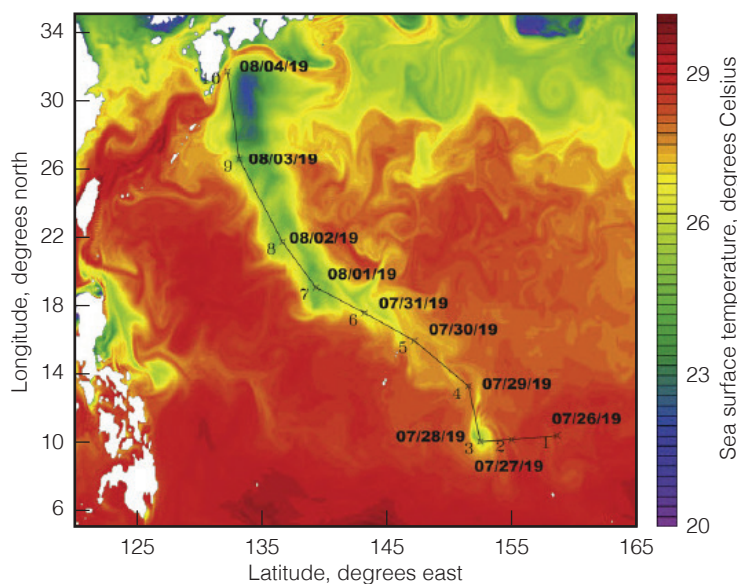
Livermore finite-volume simulation



sources of prediction uncertainty, as well as to assess low-probability but high-consequence events such as rapid melting of the polar ice sheets.

Livermore Grand Challenge simulations and calculations helped lay the foundation for new climate research efforts, most notably the Accelerated Climate Modeling for Energy initiative, launched in 2014 by the Department of Energy's Office of Science. Over the next decade, the initiative's academic, industry, and government partners, including Lawrence Livermore, will expedite the development and testing of models for climate and energy applications. This work is done in anticipation of new and disruptive HPC architectures, such as those to be delivered through the Collaboration of Oak Ridge, Argonne, and Livermore in 2017 and 2018 and the exaflop-scale machines likely to follow. (See *S&TR*, March 2015, pp. 11–15.) These models will have the same resolution as Bader's Grand Challenge simulation but will be more sophisticated and computationally demanding Earth system models. "Earth system models are the future," says Bala. "These are models that include carbon, nitrogen, sulfur, and phosphorous cycles besides the usual physical components."

States Bader, "The big challenges for climate modeling are actually harder now than those we faced a decade ago. Climate scientists have shown that climate change is real, increasing, and potentially irreversible. Now policymakers are asking for tools to predict the rate of change and answer other hard questions." Climate scientist Ben Santer adds, "We know that Earth's climate system is going to experience profound changes, such as large-scale warming and moistening of the atmosphere, rising sea levels, retreat of snow and sea-ice cover, and increases in the frequency and intensity of heat waves, but the regional and seasonal details of these changes are much fuzzier." Predicting these details with precision and confidence and delivering information that can help countries and communities



This ultrahigh-resolution global simulation of present-day climate conditions was detailed enough to track the progress of a Category 4 hurricane and its associated wake of cold water in the tropical northwest Pacific. Modeling extreme climate events is an important capability, as their frequency and intensity is expected to be increased by climate change.

make resource-planning decisions will require enhanced models and exaflop-scale computing capabilities.

### Building on a Decade of Success

By most any measure, the Grand Challenge Program's inaugural decade has been a success. The program has seen steady growth in proposals and time requested, and the quality of ideas evaluated each year by internal and external referees has been consistently high. Furthermore, many boundary-pushing concepts have gone on to become new, robust programs or projects or to boost existing ones. Multiprogrammatic and Institutional Computing Program director and Grand Challenge Program co-lead Brian Carnes notes, "When a project is granted significant HPC resources to fully develop its science and technology, that's when it starts having value. The Grand Challenge Program allows that value to develop, so that it can be impactful to the programs." Pacific Northwest, Los Alamos, and Sandia national laboratories have also created their own Grand Challenge-type programs modeled on Lawrence Livermore's.

The Grand Challenge Program represents a sizeable investment of the Laboratory's

computing time. In fact, only six countries in the world possess more computing resources than Livermore makes available to individual researchers and programs for unclassified computing through the Multiprogrammatic and Institutional Computing Program initiatives, including the Computing Grand Challenge Program. These investments pay dividends by advancing challenging and mission-relevant research and honing the skills of researchers through access to new computational architectures and modeling and simulation methods.

—Rose Hansen

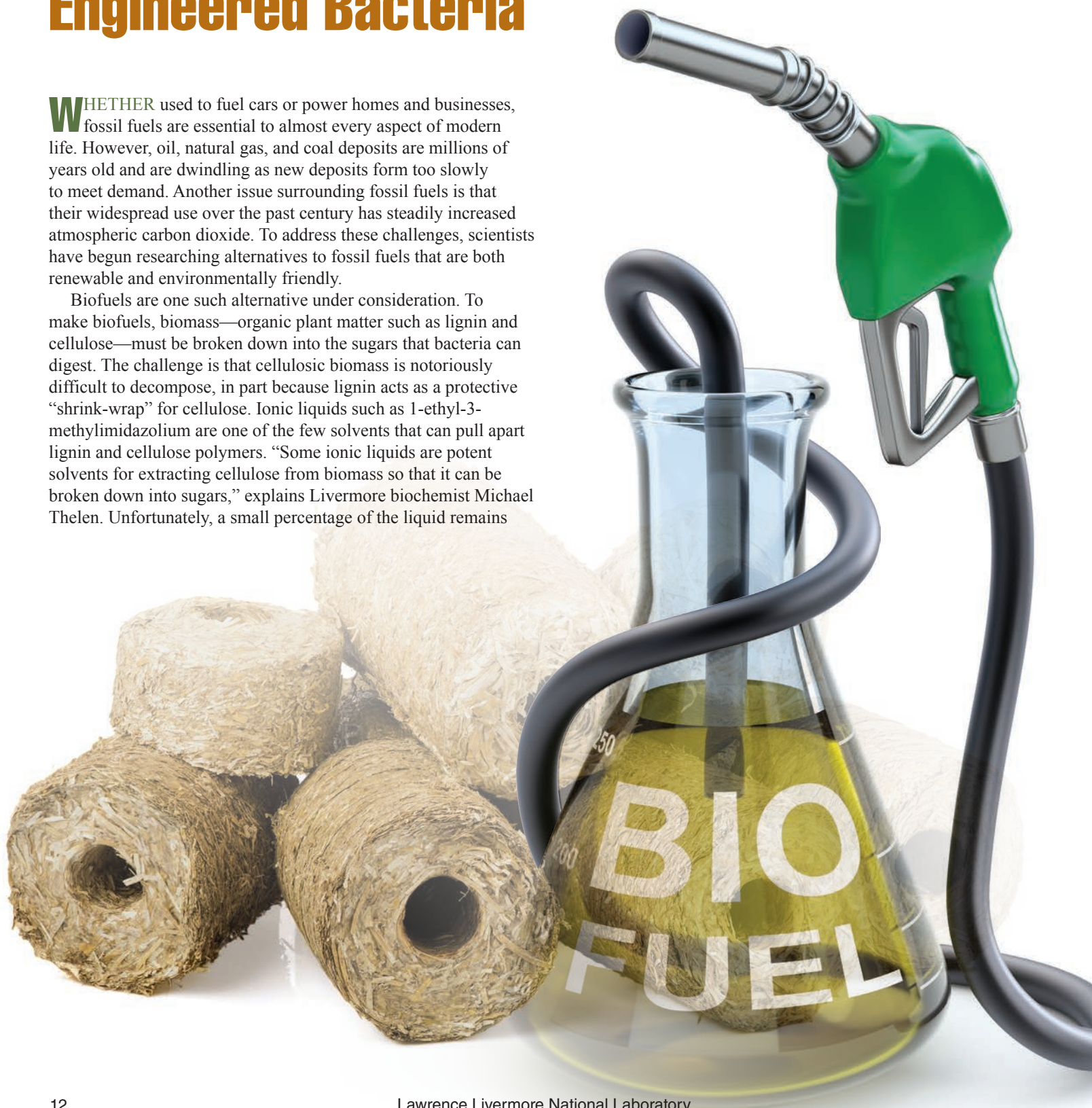
**Key Words:** Accelerated Climate Modeling for Energy, Atlas, climate model, Community Climate System Model (CCSM), Computing Grand Challenge Program, Dawn, density functional theory (DFT), Earth system model (ESM), exaflop, first-principles model, high-performance computing (HPC), hohlraum, laser-plasma interaction (LPI), molecular dynamics (MD), Multiprogrammatic and Institutional Computing Program, National Ignition Facility (NIF), petaflop, Qbox, quantum Monte Carlo (QMC), Sierra, teraflop, Thunder, uncertainty quantification, unclassified computing, Vulcan.

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# Biofuel Breakthrough with Engineered Bacteria

**W**HETHER used to fuel cars or power homes and businesses, fossil fuels are essential to almost every aspect of modern life. However, oil, natural gas, and coal deposits are millions of years old and are dwindling as new deposits form too slowly to meet demand. Another issue surrounding fossil fuels is that their widespread use over the past century has steadily increased atmospheric carbon dioxide. To address these challenges, scientists have begun researching alternatives to fossil fuels that are both renewable and environmentally friendly.

Biofuels are one such alternative under consideration. To make biofuels, biomass—organic plant matter such as lignin and cellulose—must be broken down into the sugars that bacteria can digest. The challenge is that cellulosic biomass is notoriously difficult to decompose, in part because lignin acts as a protective “shrink-wrap” for cellulose. Ionic liquids such as 1-ethyl-3-methylimidazolium are one of the few solvents that can pull apart lignin and cellulose polymers. “Some ionic liquids are potent solvents for extracting cellulose from biomass so that it can be broken down into sugars,” explains Livermore biochemist Michael Thelen. Unfortunately, a small percentage of the liquid remains



bound to cellulose during its breakdown to sugars and, even at low residual levels, is toxic to biofuel-producing bacteria and yeast.

In research conducted at the Joint BioEnergy Institute (JBEI) in Emeryville, California, a Livermore team led by Thelen has discovered a gene that enables bacteria to survive in the hostile environment of an ionic-liquid solvent, thus overcoming a major bottleneck to efficient biofuel production. Notes Thelen, “Growing demand for energy and finite availability of oil and gas motivates the serious consideration of alternatives. Lignocellulose biomass feedstock offers the best substitute as a sustainable and renewable fuel source.”

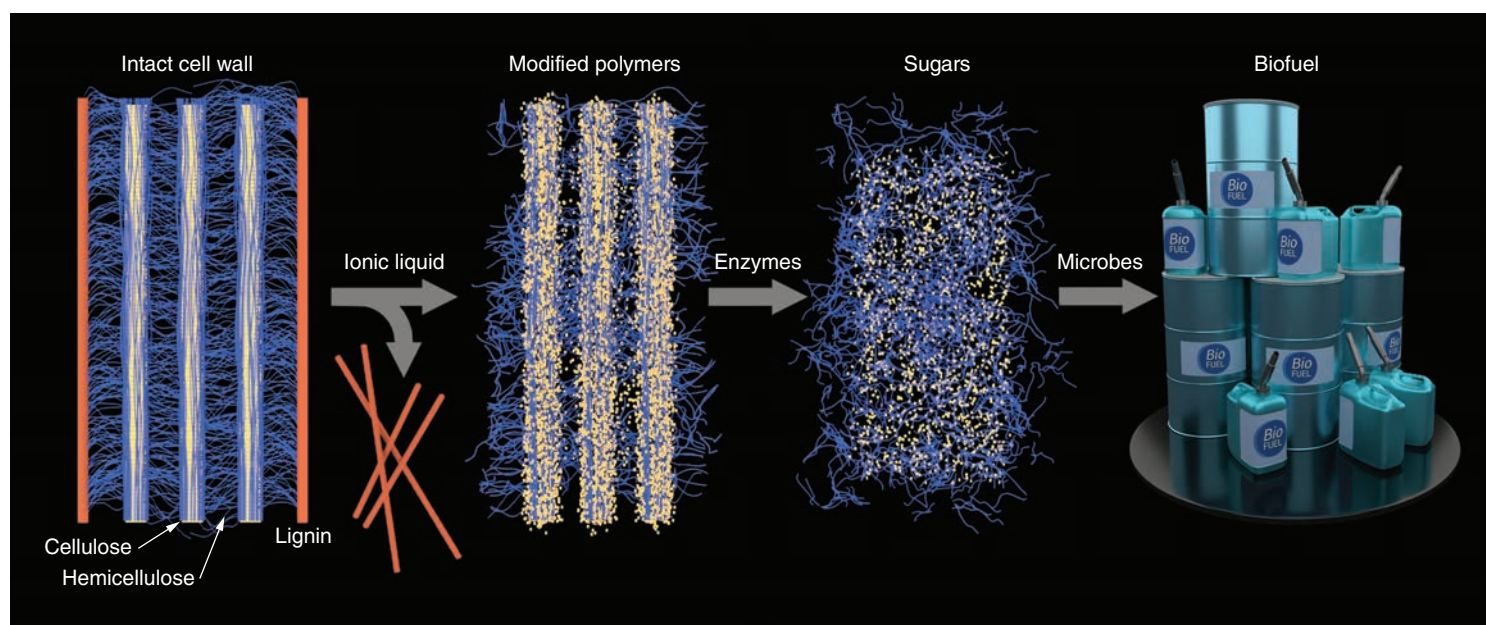
### Engineered Pathways

The intestinal bacterium *Escherichia coli* and brewers yeast are the two most widely used microbes for producing biofuels because of their well-known genetics and biological pathways. One of JBEI’s objectives is to prepare plant biomass using ionic liquids and to engineer bacteria with novel pathways for producing biofuel. Because *E. coli* and yeast cannot tolerate residual ionic liquids in their sugary feedstock, the microbes must be engineered to process the solvents differently. “To overcome this problem,

we have to look at other mechanisms in nature and then choose genes to design the best one for bacteria to create biofuels,” explains Thelen.

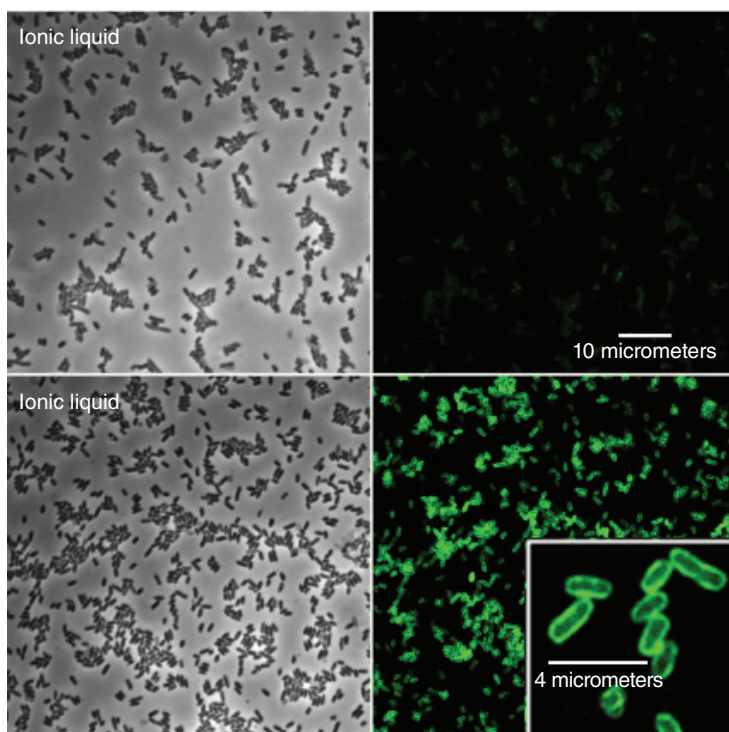
The team’s first step was to identify why ionic liquids are so toxic to *E. coli* and yeast. “We started out looking at two different microbial communities in nature that could possibly contain enzymes that break down biomass better than the standard bacteria used in lab experiments,” says Thelen. “We wanted enzymes that were thermotolerant and stable in high-salt environments.” They found such microbes in the rain forests of Puerto Rico, where bacteria help degrade leaves and plant matter on the forest floor. According to Thelen, similar bacteria can be found in green waste compost from commercial facilities.

The team performed various tests—including phenotypic growth assays, phospholipid fatty acid analysis, and RNA-sequencing techniques—to screen the rain forest microbes for molecular mechanisms that may sustain them in ionic-liquid media. “In nature, bacteria do not live in a vacuum but rather compete and cooperate with one another,” notes Thelen. “Understanding how they interact within an environment can help us apply their natural processes for other scientific purposes, including biofuel production.”



The first step in biofuel production is to break down biomass—organic plant matter such as lignin and cellulose—into sugars. Ionic liquids, such as 1-ethyl-3-methylimidazolium, are potent solvents that solubilize organic matter and separate it into fragments to be further broken down with enzymes into sugars. Engineered bacteria then use these sugars to create biofuel. (Rendering by Ryan Chen.)

The researchers studied gene expression patterns in the soil bacterium *Enterobacter lignolyticus*, using a sequencing analysis technique known as transcriptomics. They found that ionic-liquid resistance was related to how bacteria direct substances through their membrane. Using sophisticated genomic tools in collaboration with the Department of Energy's Joint Genome Institute (JGI), the researchers studied the molecular and physiological response of a strain of *Enterobacter* and looked at all the genes being activated when the bacteria were exposed to different levels of ionic liquids. They determined that *E. lignolyticus* could survive in much higher salt concentrations than the standard laboratory microbes. Delving further into the relevant metabolic biological pathways, the team analyzed which genes became more active (were upregulated) and which genes became less active (were downregulated) when the bacteria were coping with ionic liquids. Former Livermore postdoctoral researcher Jane Khudyakov found trends that pointed to survival mechanisms, including the upregulation of genes responsible for transporting small molecules across cell membranes.

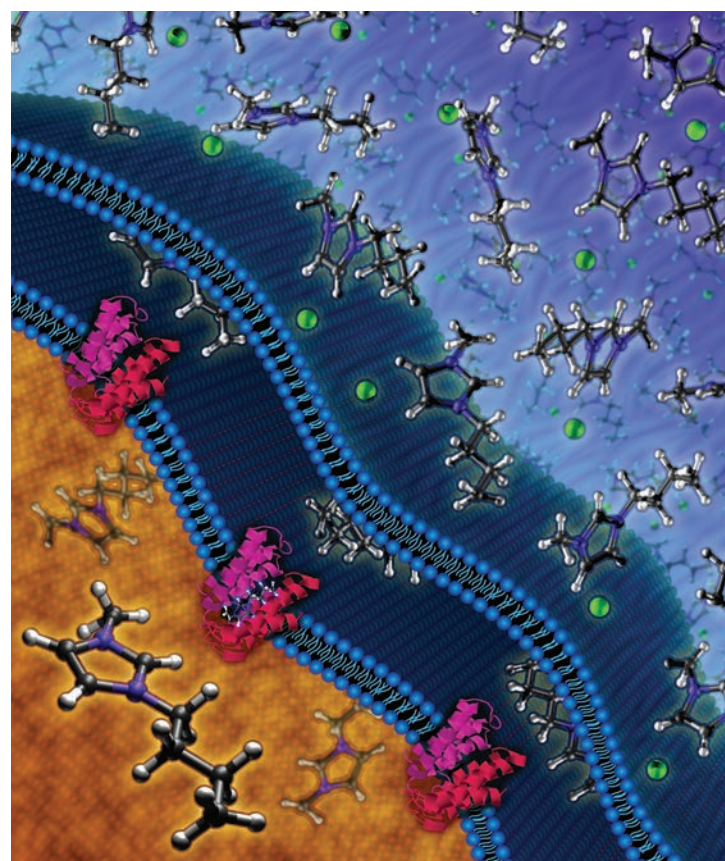


(left) Phase contrast and (right) fluorescence microscopy images show that compared to (top row) an ionic-liquid-free environment, *Escherichia coli* cultures thrive in an otherwise toxic environment of (bottom row) the ionic liquid 1-ethyl-3-methylimidazolium chloride. This breakthrough happens because the biofuel bacteria express a fusion protein from a plasmid carrying the regulator gene. The inset shows membrane localization of the transporter gene.

### A Single Gene Holds the Key

The innate ability of *E. lignolyticus* to thrive in the presence of ionic liquids led the researchers to theorize that a complex mechanism involving potentially many genes was involved. To reveal the elusive mechanism, the team used an approach devised by Thelen's graduate student Thomas Ruegg from Basel University, in which he examined *E. lignolyticus* DNA by comparing approximately 25 different DNA fragments, each of which has the same level of ionic-liquid tolerance when transferred to *E. coli*.

The team analyzed chunks of *E. lignolyticus* incorporating 30–50 kilobases of DNA to create a genomic library of the bacterium. In this process, DNA was extracted, cloned, and introduced into *E. coli*. "With this method, we can sample much



Ionic-liquid-tolerant microbes use efflux pumps to export ionic-liquid molecules from inside a cell, as interpreted by this artist's rendering. The microbes use these protein structures (red and magenta) embedded in the inner cellular membrane (blue sheets of lipid bilayers) to help them grow in the presence of inhibitory concentrations of the ionic liquid 1-ethyl-3-methylimidazolium. (Rendering by Mona Aragon, Sandia National Laboratories.)

larger bits of DNA,” explains Thelen. “If you take a long enough stretch of the DNA, it can represent a complete biochemical pathway that produces the response you are trying to identify.” The method enabled the researchers to see how and when the different genes were activated and how they influenced one another.

The researchers discovered two adjacent genes that were common to all of the genome fragments. “One of these genes matched an upregulated gene found in the transcriptome data that affects a membrane transport protein called a multidrug efflux pump. We concluded this pump must transport ionic liquid out of the cell interior, and that this single gene was sufficient to promote ionic-liquid tolerance in *E. coli*,” Thelen explains. The second gene corresponded to a regulator, or switch, that senses the level of ionic liquid and in response turns on and off the production of its neighboring pump gene.

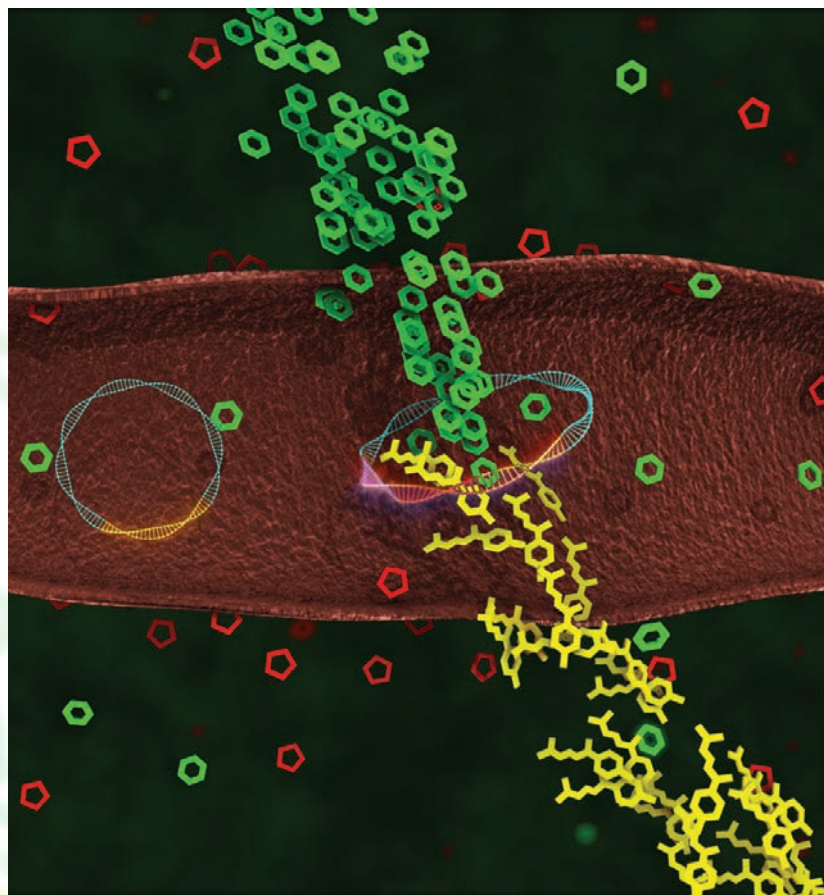
After tests showed that *E. coli* had the same tolerance as *E. lignolyticus*, the team characterized the transporter and how it was regulated. Ruegg explains, “We verified that the transporter and regulator were indeed responsible for ionic-liquid tolerance. The regulator gene responds directly to external concentration of ionic liquid, adjusting the level of transporter needed to enable robust growth and biofuel production when the liquid is left in sugars from pretreated biomass.”

Using the newly engineered *E. coli*, the researchers efficiently produced the biofuel precursor bisabolene in laboratory-scale experiments, successfully demonstrating that ionic-liquid resistance can be engineered into fuel-producing bacteria. In addition, their work revealed that a bacterial regulator can be turned on and off, generating pumps only when the cells are exposed to ionic liquids and not before. As a result, cells can conserve their energy for other biological functions, including more rapid growth. Thelen and his team are exploring this switching mechanism as a way to control genes other than the pump, including the genes that trigger fuel production.

### Paving the Way Forward

The collaboration among Livermore, JGI, and JBEI demonstrates how partnerships can lead to great advances in areas that are important to the nation and to peoples’ everyday lives. “As a result of our study, we have shown that *E. coli* can grow in the presence of normally toxic levels of an ionic liquid, making it possible to produce biofuels more efficiently,” summarizes Thelen. “Our work paves the way for further improvements in the microbial conversion of biomass to biofuels. Such an advance is desperately needed to reduce our dependence on fossil fuels; create sustainable, home-grown energy resources; and ensure energy security for our nation.”

The team plans to focus on researching the metagenomic data from many different microbes to create a library with which they



This rendering illustrates the rapid conversion of biomass-derived glucose to a chemical compound that bacteria would normally not synthesize. Inside the cell, a ring-shaped DNA plasmid (left) has the single gene to produce an efflux pump, enabling growth in the presence of toxic levels of ionic liquid (red pentagons). The other plasmid (right) contains enzyme-encoding genes to convert glucose (green hexagons) to the biofuel precursor bisabolene (yellow). (Rendering by Kwei-Yu Chu.)

can further engineer bacteria for biofuels. With every advance in biofuel production, the nation takes another step toward energy independence with reduced environmental impact.

—Caryn Meissner

**Key Words:** biofuel, bisabolene, cellulosic biomass, efflux pump, energy independence, *Enterobacter lignolyticus*, *Escherichia coli*, ionic liquid, Joint BioEnergy Institute (JBEI), Joint Genome Institute (JGI).

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# Supercapacitors Yield Energetic Secrets

**I**N the race for advanced energy storage systems, researchers are increasingly turning to the supercapacitor, a seemingly straightforward device made attractive by its many advantages over most batteries, including higher power density, faster charge–discharge cycling, enhanced safety, lower cost, and better endurance. Dynamic processes at the interfaces between electrodes and electrolytes are essential for supercapacitors to operate efficiently, but not enough is known about these interfaces to improve the capabilities of supercapacitors. This is where Livermore researchers are making key strides in understanding this critical energy technology.

The paucity of knowledge about supercapacitors persists because of the technical challenges involved in monitoring their electrode–electrolyte interfaces during operation. Yet this area is precisely where detailed understanding is needed to design more efficient devices for practical, widespread use. To expose the details of operating supercapacitors, a Livermore-led team developed a new experimental capability in x-ray absorption spectroscopy (XAS) and coupled the results to improved methods for quantum-mechanical modeling and simulation.

This tightly coupled experiment-and-modeling approach enabled Livermore researchers to measure, for the first time, the dynamic changes that occur in the electronic structure of graphene supercapacitor electrodes as they charge and discharge. The measurements—published as the cover article of the March 4, 2015,

An artist's rendering shows an x-ray photon entering the experimental cell (upper left) at the Advanced Light Source, illuminating a hydroxyl ion ( $\text{OH}^-$ ). The  $\text{OH}^-$  ion, disassociated from an aqueous solution of sodium chloride, has bonded to a carbon atom, forming part of a supercapacitor electrode made of sheets of graphene aerogel. The  $\text{OH}^-$  ion is colored red and is bonded to a white hydrogen atom to its immediate right. This achievement was featured as the cover story of the March 4, 2015, issue of the journal *Advanced Materials*. (Rendering by Ryan Chen.)

issue of the journal *Advanced Materials*—revealed two unexpected phenomena contributing to capacitive charge storage.

These findings bolster scientific understanding of how carbon-based electrodes store charge at the electrode–electrolyte interface. The results contradict conventional models and suggest strategies to optimize electrodes for their surprisingly complex operational state. More broadly, the results demonstrate the potential of using the new Lawrence Livermore in situ technique to study other important materials for energy storage.

The supercapacitor effort brought together Lawrence Livermore electrochemists, physical chemists, materials scientists, physicists, and theory and simulation experts, along with colleagues from Lawrence Berkeley National Laboratory. A substantial portion of the research was supported by the Laboratory Directed Research and Development Program.

Says Livermore chemist Jonathan Lee, “Our aim was to obtain an improved understanding of the physical and chemical processes involved in electrode operation.” Lee notes that a significant amount of research has been conducted on supercapacitor electrolytes, but until now only limited experimental work sought to characterize operating electrodes, even for widely used materials such as graphite. Supercapacitor electrodes were considered to be static, with charge accumulation or depletion being the only responses to polarization of the electrode–electrolyte interface. The limitations of this view of the electrode’s behavior largely reflected a previous lack of experimental and theoretical methods to characterize electrodes under operating conditions.

The Livermore-led team turned to XAS as a powerful technique to measure the changing electronic structure of operating graphene electrodes. Their XAS measurements revealed two unexpected features—covalent (that is, chemical) bonding between the negative ions and the otherwise inert carbon electrode surface, along with local stresses and strains that change electrode bonding and morphology. These two distinct phenomena were also found to have different behaviors in time—one nearly instantaneous, the other taking many minutes. In addition, both processes were largely reversible once charging stopped, explaining why they could only have been observed during operation.

### Aerogels Bolster Supercapacitor Advantage

The Laboratory’s findings have gained widespread attention in the energy world because of the growing hopes being pinned on supercapacitors. A capacitor stores energy by means of a static charge instead of an electrochemical reaction. Whereas a conventional capacitor is made up of positively and negatively charged conductive materials separated by an insulator, supercapacitors contain no solid insulator. Instead, two conductive, high-surface-area solids are immersed in an electrolyte solution. When a voltage is applied across the positive and negative plates, the negative electrode attracts positive ions from the solution, while the positive electrode attracts negative ions, charging the supercapacitor.

“Because of the large surface area and the atomic-scale distance between the ions and the electrode surface, carbon electrode supercapacitors can hold hundreds of times the electrical charge as standard capacitors and can therefore serve as a replacement or companion for batteries in many industrial and commercial applications,” states materials scientist Juergen Biener. Supercapacitors can also undergo frequent charge and discharge cycles at high current and short duration—an important property for meeting peak loads for electric vehicles or grid-scale demands, such as farms of wind turbines.

For the electrode material, Livermore scientists turned to graphene aerogel, which Livermore researchers have pioneered for

more than 30 years. In particular, Lee and his team focused on a three-dimensional nanographene bulk electrode material consisting of crumpled sheets one to three layers of carbon atoms thick. Says chemist Ted Baumann, “Being built from single-layer graphene sheets gives graphene aerogels the highest internal surface area of any pure carbon material—nearly 3,000 square meters per gram.” (See S&TR, April/May 2015, pp. 14–18.) This is key because the higher the surface area to store ions on both sides of the graphene sheets, the higher the overall charge storage capacity. Compared to traditional carbon-based electrodes, graphene aerogels also offer greater control of density and pore-size distribution, from 1 nanometer to several micrometers in diameter. Furthermore, conductivity is increased through interconnectedness of the carbon sheets and the absence of nonconductive binder materials.

### Seeing the Light

Probing the processes involved in graphene electrode operation presented “huge engineering challenges,” notes materials scientist Michael Bagge-Hansen, the first author of the *Advanced Materials* paper. The biggest challenge was conducting in situ XAS experiments on the Advanced Light Source (ALS) synchrotron at Lawrence Berkeley. To provide monochromatic x rays, the ALS generates a hair-thin ( $0.20 \times 0.01$  millimeter) beam of electrons and accelerates them first in a linear accelerator and then in a booster ring to nearly the speed of light, causing the electrons to emit x-ray light 1 billion times brighter than the Sun. Directed to an experimental apparatus, the light interrogates the electronic structure of matter.

The Livermore team was already adept at XAS for studying the unoccupied electronic structure of elements in vacuum environments. XAS is extremely sensitive to changes in electron structure in ways that more traditional techniques cannot approach. Because carbon is a low-atomic-number element having only six protons, the appropriate x rays are low energy or “soft,” about 300 electronvolts. Soft x rays will not transmit through air, so experiments must be conducted under vacuum.

To measure the electrode material under in situ operating conditions, however, a fluid electrolyte was required. Lee therefore marshalled an effort to design and build a vacuum-compatible cell 2 centimeters in diameter and featuring a tiny supercapacitor measuring about 5 millimeters tall and 0.1 millimeter thick. The electrolyte was a standard 1 molar aqueous solution of sodium chloride.

The cell incorporated an x-ray window of silicon nitride only 100 nanometers thick (or a hundredth of the thickness of a human hair). The window separates the ultrahigh vacuum of the analysis chamber from the fluid electrolyte environment of the supercapacitor while allowing x rays to pass in and out of the sealed experimental cell, for detection of both x-ray absorption

and emission. The ultrahigh vacuum environment, with a pressure of  $10^{-9}$  torr (approaching that found in deep space), ensured that the soft x rays did not interact with air.

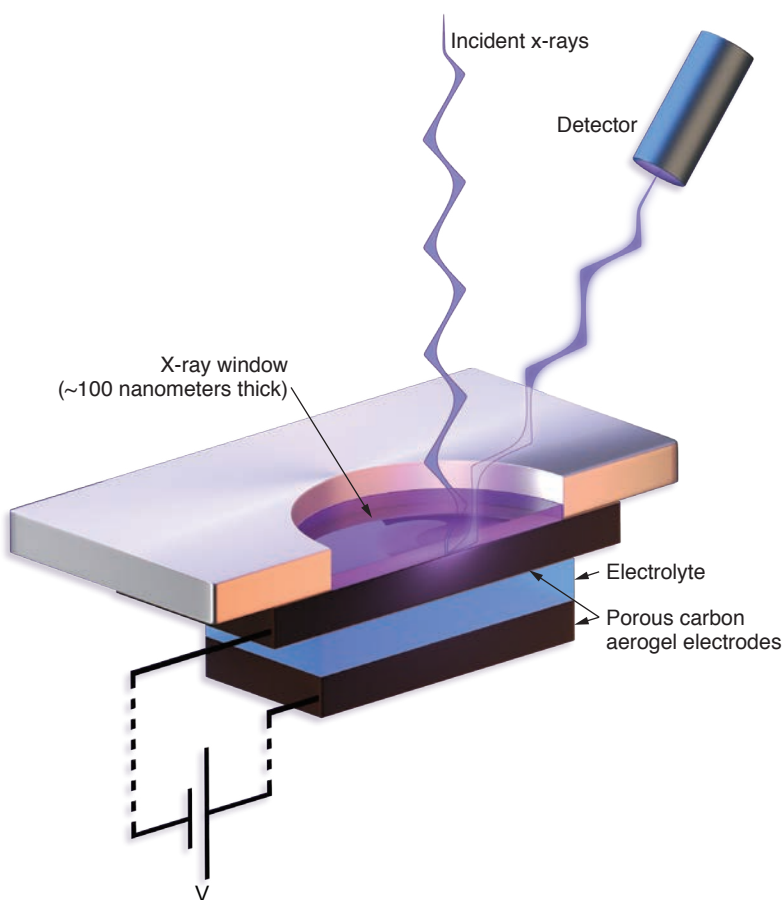
Probing the graphene aerogel with XAS, the researchers consistently saw two peaks corresponding to two events occurring on the positive graphene electrode. (No peaks were evident during the charging or discharging of the negative electrode.) Incoming x rays temporarily promote some of the carbon atoms' electrons to higher unoccupied electron states, leaving behind a hole. These

excited carbon atoms can return to a lower or ground state as electrons from filled states drop into the holes. When this happens, photons of particular wavelengths are emitted and can be detected as a function of incident x-ray energy, revealing the carbon's electronic structure. In short, the recorded peaks in photon intensity provide information about specific, significant physiochemical phenomena in the electrode.

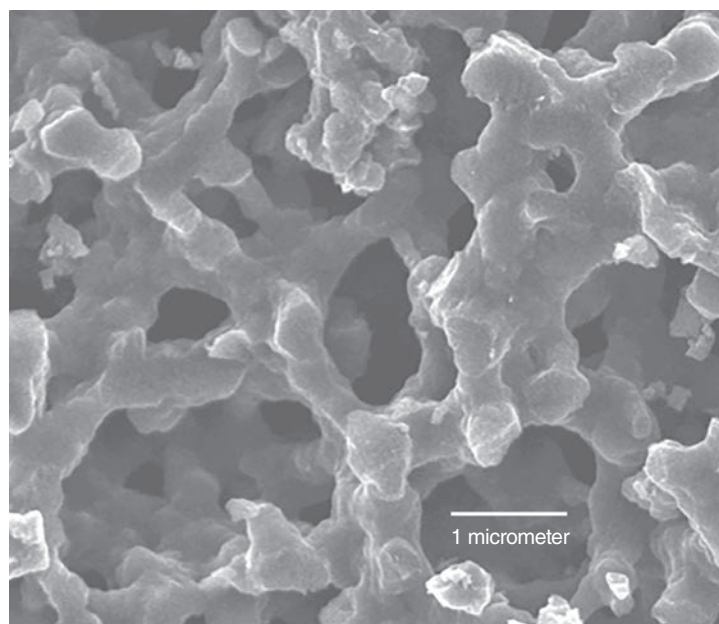
## Two Surprises

To elucidate the mechanisms behind the two XAS signatures, Lee and his team brought in Livermore experts in advanced modeling and simulation, led by materials scientists Brandon Wood and Tadashi Ogitsu. One recorded peak was consistent with adsorption of a specific anion—a negatively charged ion—on the positive electrode surface. Wood and Ogitsu showed that this peak represented the nearly instantaneous adsorption of hydroxyl ions ( $\text{OH}^-$ ) from water molecules to the carbon atoms.

The sudden binding of  $\text{OH}^-$  from the dissociation of water molecules, rather than chloride ions, was a surprise to the team. The reaction is reversible—the ions return to solution upon removal of the applied voltage. The reversible adsorption of  $\text{OH}^-$  upon charging corresponded to a different means of storing charge



To enable measurements of supercapacitor electrodes while they operate, Livermore researchers built a vacuum-compatible cell that measured 2 centimeters in diameter and contained a tiny supercapacitor (5 millimeters tall and 0.1 millimeter thick) placed in an aqueous solution of sodium chloride, the electrolyte. The cell incorporated a window of silicon nitride 100 nanometers thick that lets x rays pass through the cell to permit detection of both x-ray absorption and emission. Although appearing solid in this illustration, the electrode is extremely porous to permit the buildup of large amounts of electrical charge at the electrode–electrolyte interface.



This scanning electron microscope image shows the extremely complex structure of a nanographene aerogel making up the Lawrence Livermore supercapacitor electrode. The gaps represent large pores, while crossing branches called ligaments possess much smaller pores. The interconnectedness of the carbon sheets increases electrical conductivity.

called pseudocapacitance, in which a direct chemical bond forms on the electrode surface and adds to the supercapacitor's total stored charge. "The observation of pseudocapacitive interactions, particularly the identification of the specific anion involved, was beyond our initial expectations," Lee emphasizes.

The second—and larger—peak at higher energies reflected a process unfolding on a much longer timescale—20 to 30 minutes. Lee explains that the electrodes of extremely thin sheets of graphene are not straight, instead resembling wrinkled or rippled pieces of paper combining to form larger intersecting structural features called ligaments. The resulting structures have pores with diameters ranging from the nanometer to micrometer scales.

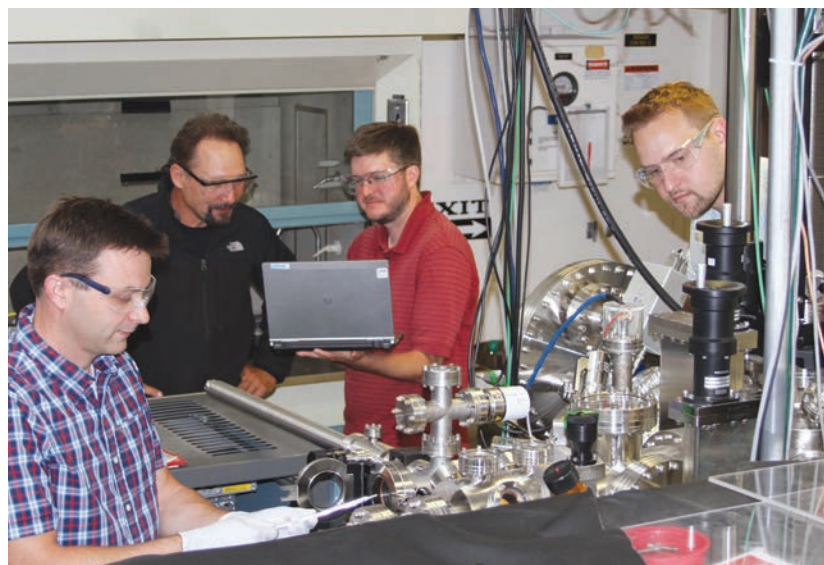
Charging occurs preferentially along the surfaces of larger pores because they offer the least resistance to diffusion. A thin layer of ions accumulates at the electrolyte–electrode interface, which serves as the primary source of charge storage in the system, as expected for a supercapacitor. However, the small, nanometer-scale pores provide much higher resistance to flow of ions in the electrolyte, and the pores' electrode–electrolyte interface takes longer to come into equilibrium.

Wood and Ogitsu's models indicate that different rates of ion flow and charge storage are locally experienced as tensile stress between neighboring pores, which initiates local planarization (flattening) of the graphene sheets. In effect, the electrode becomes stretched, removing some wrinkles and flattening the thin sheets of graphene. The phenomenon is indicated by the second spectral peak. Upon full charging, this stress gradient is partially neutralized. "We think that stress builds up initially, then dissipates slowly," explains Wood. Small areas of the sheets transition between rippled and stretched as the associated strain works its way throughout the electrode over approximately 30 minutes.

"Livermore's novel theoretical approach much more closely represents what is actually being measured and can serve as a direct interpretation of experiments," Wood comments. He explains that typically, scientists attempt to match experimental results with more conventional theoretical computations of electronic structure and make educated guesses. Instead, the Livermore method directly simulated the ALS experiments, including the applied voltage and the interaction of x rays with the graphene electrodes.

### Profound Changes

"A lot of intellectual effort across various scientific disciplines was required to figure out what was going on," notes Bagge-Hansen. "Our research findings were more complicated than we anticipated." The results, he says, were both "unexpected and not obvious." He also says that because both effects are transient and reversible, and are related to the specific interaction between the electrodes and the liquid electrolyte, "we would never have seen these two effects without monitoring operating electrodes."



(left to right) Livermore researchers Jonathan Lee, Juergen Biener, Brandon Wood, and Michael Bagge-Hansen test cell components for ultrahigh vacuum capability at Livermore in preparation for x-ray spectroscopy measurements of supercapacitor electrode behavior at Lawrence Berkeley's Advanced Light Source (ALS). The intense x-ray light at ALS—1 billion times brighter than the Sun—enabled the team to uncover previously unknown behavior.

Overturning the once generally held theory that graphene-based supercapacitor electrodes are electrochemically inert, the team demonstrated that they undergo profound changes during operation. Their research shows how capacitance and charge storage are not solely determined by the isolated properties of the electrode and electrolyte but rather are strongly influenced by electrode modifications that occur during charging and discharging.

Energy experts at Livermore declare that this more complete understanding of how operating supercapacitor electrodes function could lead to new and better strategies for improving the capacity and efficiency of supercapacitors and hasten their adoption in real-world energy storage applications everywhere, to the benefit of energy consumers the world over.


—Arnie Heller

**Key Words:** Advanced Light Source (ALS), battery, electrode, graphene aerogel, Laboratory Directed Research and Development (LDRD) Program, Lawrence Berkeley National Laboratory (LBNL), supercapacitor, x-ray absorption spectroscopy (XAS).

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# UNDER PRESSURE

## Granular Studies with Immeasurable Implications



Livermore researcher Hye-Sook Park holds a gold hohlraum used in National Ignition Facility laser experiments to test the strength of tantalum at a previously unobtainable combination of pressure and strain rate. Similar hohlraums were used in experiments at the Omega Laser Facility to study the dependency of the metal's grain size on its strength. The findings revealed that the grain size–strength relationship, thought to be universal as expressed by the Hall–Petch equation, broke down under the extreme conditions. This important finding has key ramifications in the Laboratory's ongoing work related to the nation's nuclear stockpile. (Photograph by Lanie L. Rivera.)

**I**n the age-old practice of blacksmithing, a smith heats a piece of metal until it becomes malleable and then shapes it with a hammer, anvil, or other tool. What ancient practitioners of this art knew from experience we now know scientifically: Heating and pounding affect the metal at a microscopic level by changing the size of its grains and introducing defects into the crystal. Smaller grains have more surface area in contact with neighboring grains, and these grain boundaries impede plastic flow when force is applied. The strengthening of a material by changing its grain structure is described by the Hall–Petch equation, which specifies the relationship between grain size and strength.

Hall–Petch conventionally indicates that smaller grain size translates into stronger material, but Livermore researchers have recently found evidence that this relationship does not hold true in the domain of extremely high pressures and strain rates—pressures greater than 100 gigapascals (GPa), compared to pressure at Earth’s core of roughly 350 GPa, and strain rates of approximately  $10^7$  per second. In a series of 30 high-energy tantalum experiments conducted on samples of various grain sizes at the University of Rochester’s Omega Laser Facility, the researchers found the surprising result that grain size did not influence material strength in that extreme regime.

### Steps to Success

Lawrence Livermore has a longstanding need to understand materials at extreme conditions because of its mission in the science-based stewardship of the nation’s nuclear stockpile. Tantalum, the focus of the recent materials strength experiments, is a model body-centered-cubic, ductile metal that serves as an ideal test of scientific understanding of high-pressure material response, without the complexities of a phase transition. (See S&TR, December 2000, pp. 4–11). The material is also an area ripe for further research. “When our team found that little was known about

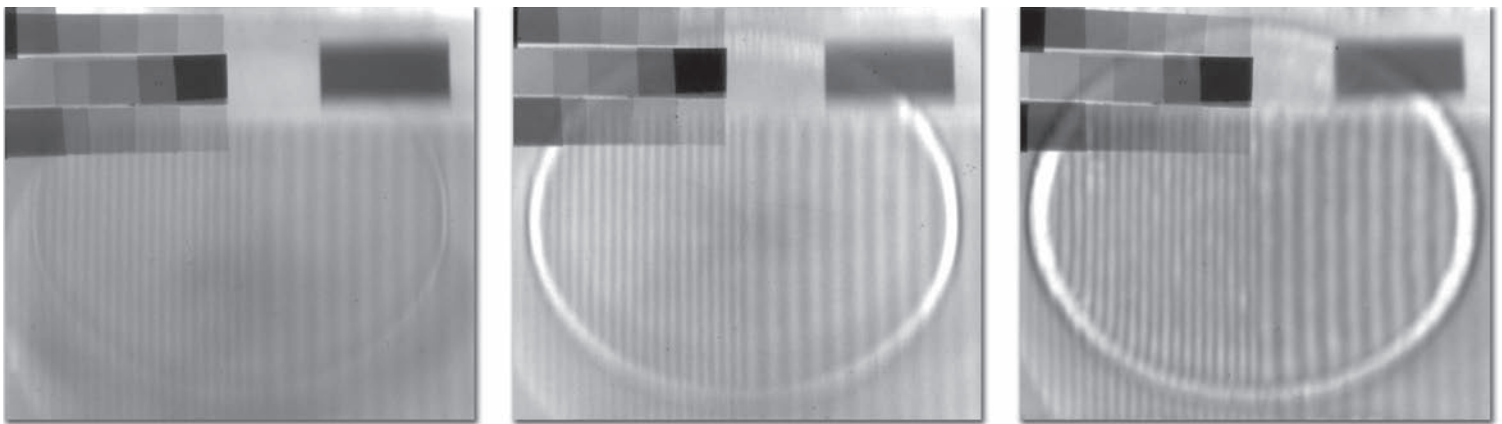
materials’ strength under extreme conditions, we were motivated to explore this realm,” says Robert Rudd, who led the project’s multiscale modeling effort.

The Livermore materials strength tests were the first to be done in this regime, as they had been considered infeasible by many researchers. “The notion of being able to study grain-size effects was extraordinary,” explains Rudd, “because it requires such a high level of precision to accurately see changes in material deformation.” Creating this new capability required closely coordinated development of target components, diagnostic tools, and a Livermore multiscale strength model. “Preparation for the experiments demanded a long-term vision with many years of research and innovation,” states physicist Hye-Sook Park, who led the Livermore experimental team.

### A Ripple Effect

During the Omega experiments, 40 finely tuned laser beams simultaneously struck a 7-millimeter-long hohlraum, a gold cylinder with a hole at each end, thereby creating an “oven” of x-ray radiation inside. Positioned over a third hole in the hohlraum’s side was a 2-millimeter-thick physics package with a layered sample containing tantalum. The radiation heated the physics package, building pressure against the sample.

To deduce the strength of tantalum under applied pressure, the team measured the growth of pre-imposed sinusoidal ripples on the sample through a phenomenon called Rayleigh–Taylor instability. This instability occurs naturally when acceleration (pressure) is applied to a material interface that has different densities. When the material is strong, the ripples will grow, but their growth rate will be slower than that of a weaker material’s ripples. The amplitude of ripple growth was measured with face-on radiography, in which greater contrast from peak to valley indicates greater growth. A similar approach was also utilized for high-explosive experiments



Radiographs show Rayleigh–Taylor ripple growth in tantalum subjected to laser beams at three different delay times—40, 55, and 75 nanoseconds (left to right). The delay time is the time difference between when the laser drives the tantalum sample and when the backlighter beams turn on. The higher ripple contrast exhibited at later times represents how the ripples have grown, which is used to infer sample strength.

at Los Alamos National Laboratory and Nova laser experiments at Lawrence Livermore led by Bruce Remington.

Target fabrication was no simple task. Even state-of-the-art single-crystal diamond tools—such as a single-point diamond-turning lathe widely used to fabricate targets with high-precision features—do not work on tough tantalum because of the very high rate of tool edge wear the metal causes. Instead, materials scientist Kerri Blobaum and her team were tasked with adapting a coining or pressing technique—most notably used by the U.S. Mint to produce the nation’s metal coins—to shape the medium- and large-grained tantalum samples. Blobaum and her team found that steel, when coated with nitride, could be diamond turned with ripples to create a coining die, which in turn could precisely imprint the sample with the pattern. “Coining isn’t new, but doing it on the microscale and on tantalum is something Lawrence Livermore developed,” notes Blobaum.

### To See or Not to See

The team’s next hurdle was to develop a very bright backlighter diagnostic to capture high-spatial-resolution radiographs of the tantalum ripples. Park had spent several years optimizing

backlighters to emit x rays with high enough energy to penetrate high-density tantalum, in conjunction with spatial resolution high enough to capture changes in the small (50- to 150-micrometer-wavelength) ripples. This backlighter capability was possible using lasers with very high intensity ( $10^{18}$  watts per square centimeter or greater), high energy (1,000 joules or greater), and short pulses (100 picoseconds or less), which can expel the inner-shell electrons from the target materials and then quickly refill them by emitting high-energy x rays.

The next task was to create a large-area uniform drive that reaches high pressure gently. In the new experimental design, the physics package is exposed to radiation, the heat of which vaporizes a layer of beryllium foil, driving a shock through a gap and releasing plasma. The plasma loses speed upon reaching the sample, but when it reaches the sample the plasma accumulates again, gradually increasing pressure to 130 GPa.

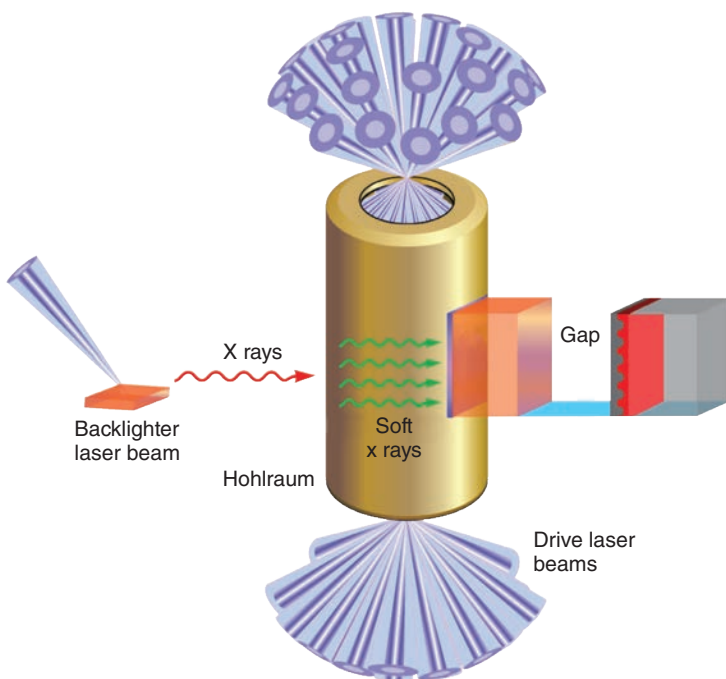
This pressure-building process, called laser-driven ramp compression, is used for high-pressure studies to avoid rapid heating, which can induce shock waves within the sample that will potentially melt and destroy its structure. (See *S&TR*, June 2009, pp. 22–23.) Raising the sample’s pressure more slowly keeps it from heating to extreme levels and melting, which would ruin the strength experiment. “Using this technique to create pressures of this magnitude with lasers is quite innovative for strength experiments,” explains Park. “Other researchers have not yet been able to do so, which explains why the validity of the Hall–Petch relation had not yet been tested at extreme conditions on different grain sizes.”

These new conditions enabled a pivotal discovery—that the inherent dislocations of a material heavily influence its strength, dwarfing contributions such as grain size (dictated by Hall–Petch) in extreme environments. This finding will have a broad effect on basic materials science theories and enable greater possibilities in Livermore’s experimental design, including the possibility—at the Laboratory’s National Ignition Facility (NIF)—of ramp-compressing a sample beyond 500 GPa without melting it.

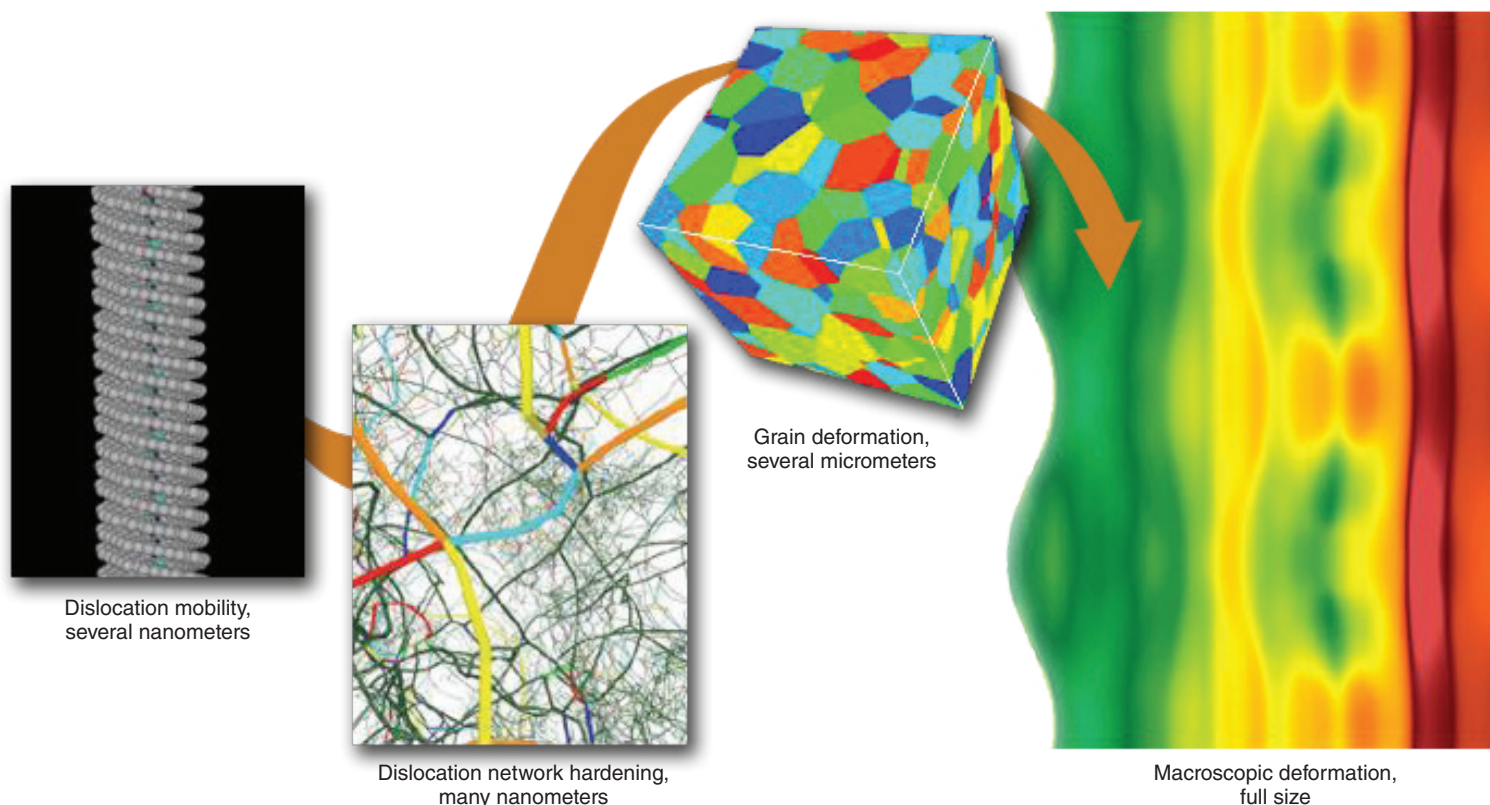
### A Model and Then Some

The Livermore multiscale strength model, which exhibits mechanical material behavior at different length scales, complemented the experimental work and helped the team gain a deeper understanding of materials at extreme conditions. At different levels, it describes fundamental stiffness, dislocations (line defects that determine a material’s strength under pressure), and the interaction of these dislocations, to calculate the macroscopic response. (See *S&TR*, July/August 2011, pp. 13–19.) Results from one modeling scale inform the next, from the atomic all the way to the macroscopic engineering level.

This comprehensive model depicts the material’s deformation patterns and plastic flow, but its initial formulation did not factor in grain size implications, which dissatisfied the scientific community,



In tantalum material strength experiments at the Omega Laser Facility, radiation from the gold hohlraum drives energy in the form of plasma across the gap. This creates a ramped-plasma drive that compresses the sample material without generating a shock that would melt the sample. Ripple growth is measured by a high-resolution, high-energy backlighter from a 5-micrometer-thick silver backlighter target.



The Livermore multiscale model can be used to understand the factors that govern how the material deforms at various length scales, including polycrystal grain size, the spacing of dislocations in the network, and the separation of atoms around the dislocation cores. Information is passed from each level to the next higher one. The model complemented the experimental work and helped the team gain a deeper understanding of materials at extreme conditions.

explains Rudd. In response, he extended the model, leveraging a grant of high-performance computing resources under Lawrence Livermore's Computing Grand Challenge Program (see feature article beginning on p. 4). Rudd adds, "Understanding the physics of why the grain size shouldn't matter at these extreme conditions, together with the compelling evidence from highly refined experiments, moved our work beyond speculation to scientifically robust results." The new insight will benefit future tests on the relationship between grain size and strength at extreme conditions using other materials, such as lead. As Lawrence Livermore researchers grapple with the impact of the new results, they will continue to probe the limits of Hall-Petch, extending studies into nearby regimes—and more extreme conditions—to understand the full scope of this discovery.

### A Long-Term Commitment

These ultrahigh-pressure and ultrahigh-strain-rate experiments exemplify how such experimental endeavors often require long-term goals and investments. "Development of these sophisticated experimental and modeling techniques took in excess of a decade's time, and at the end of that extended effort, to discover new, unexpected material behaviors is game changing," declares Rudd.

Because Omega's pressure-generating potential is capped at 130 GPa, tantalum pressure experiments have transitioned to NIF, where intense energy levels will allow experiments to achieve well beyond 500 to 800 GPa—pressures never before reached in strength experiments. These experiments are fielding some of the largest hohlraums ever used at NIF. "We are eager to see what scientific surprises we encounter," says Park. "An array of new studies enabled by NIF's enormous energy capacity will likely reveal unexpected material properties." The frontier of tantalum and other materials important to Lawrence Livermore's research for the nation is certain to expand further.

—Lanie L. Rivera

**Key words:** grain size, Hall-Petch (H-P) relation, hohlraum, Livermore multiscale strength model, materials science, National Ignition Facility (NIF), Omega Laser Facility, Rayleigh-Taylor (R-T) instability, strain rate, tantalum, target.

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*In this section, we list recent patents issued to and awards received by Laboratory employees. Our goal is to showcase the distinguished scientific and technical achievements of our employees as well as to indicate the scale and scope of the work done at the Laboratory. For the full text of a patent, enter the seven-digit patent number in the search box at the U.S. Patent and Trademark Office's website (<http://www.uspto.gov>).*

### Patents

#### Threaded Insert for Compact Cryogenic-Capable Pressure Vessels

Francisco Espinosa-Loza, Timothy O. Ross, Vernon A. Switzer, Salvador M. Aceves, Nicholas J. Killingsworth, Elias Ledesma-Orozco  
U.S. Patent 9,057,483 B2  
June 16, 2015

#### High Strain Rate Method of Producing Optimized Fracture Networks in Reservoirs

Jeffery James Roberts, Tarabay H. Antoun, Ilya N. Lomov  
U.S. Patent 9,062,545 B2  
June 23, 2015

#### Stent with Expandable Foam

Thomas S. Wilson, Duncan J. Maitland, Ward Small, IV, Patrick R. Buckley, William J. Benett, Jonathan Hartman, David A. Saloner  
U.S. Patent 9,078,738 B2  
July 14, 2015

#### Nanoscale Array Structures Suitable for Surface Enhanced Raman Scattering and Methods Related Thereto

Tiziana C. Bond, Robin Miles, James C. Davidson, Gang Logan Liu  
U.S. Patent 9,080,981 B2  
July 14, 2015

#### High Surface Area, Electrically Conductive Nanocarbon-Supported Metal Oxide

Marcus A. Worsley, Thomas Yong-Jin Han, Joshua D. Kuntz, Octavio Cervantes, Alexander E. Gash, Theodore F. Baumann, Joe H. Satcher, Jr.  
U.S. Patent 9,082,524 B2  
July 14, 2015

#### Mechanically Stiff, Electrically Conductive Composites of Polymers and Carbon Nanotubes

Marcus A. Worsley, Sergei O. Kucheyev, Theodore F. Baumann, Joshua D. Kuntz, Joe H. Satcher, Jr., Alex V. Hamza  
U.S. Patent 9,087,625 B2  
July 21, 2015

#### Solar-Powered Cooling System

Joseph C. Farmer  
U.S. Patent 9,091,466 B2  
July 28, 2015

#### Electron Beam Diagnostic System using Computed Tomography and an Annular Sensor

John W. Elmer, Alan T. Teruya  
U.S. Patent 9,105,448 B2  
August 11, 2015

### Awards

Livermore's **Kambiz Salari** was awarded a **Distinguished Achievement Award** by the **Department of Energy Vehicle Technologies Office** in recognition of his aerodynamics research. He has led the Vehicle Systems Aerodynamic Drag Reduction Project for almost 20 years, and his work underpins commercial drag-reduction technologies for long-haul trucks. Salari's scientific research has led to significant developments in the field and has accelerated the commercialization and adoption of trailer skirts, tails, and other aerodynamic equipment on trailers today. Estimated savings from commercial trailer skirts and tails are more than 1.1 billion gallons of diesel fuel per year. In 2014, Salari's team began designing the next generation of highly aerodynamic, integrated tractor-trailers, with the goal of reducing aerodynamic drag for Class 8 trucks by 50 percent and improving fuel efficiency by 25 percent. His work is part of the Navistar SuperTruck team.

Engineers **Tom Edmunds** and **Pedro Sotorrio** received **special recognition awards** from the **Geothermal Energy Association**. Presented at the association's National Geothermal Summit, the awards recognize their work on flexible geothermal contracts, exploring economic incentives and innovative reservoir-management strategies for geothermal plant operators. Although current contracts and business practices do not provide such flexibility, "we postulate new contract structures that would allow a geothermal plant operator to switch from providing energy-only to providing flexibility to the

grid operator when it is advantageous to the plant operator to do so," Sotorrio says.

Physicist **Pierre Michel** was awarded the 2015 **Edouard Fabre Prize** for his pioneering research into energy transfer between crossing laser beams in National Ignition Facility (NIF) hohlraums. Named for one of the founders of inertial confinement fusion (ICF) in Europe, the Edouard Fabre prize is awarded to active researchers within 15 years of their doctoral degree and is sponsored by the **European Cooperation in Science and Technology Network for Inertial Confinement Fusion**. Michel was selected based on his "contributions to studying the physics of laser-driven inertial confinement fusion and physics of laser-produced plasmas." Since joining Livermore in 2006, Michel has focused on the physics of laser-plasma interactions to support the NIF ignition effort. In particular, Michel has served as the lead scientist in charge of studying and modeling cross-beam energy transfer in preparation for some of the first NIF experiments. From these studies, he successfully predicted that the implosion symmetry of fusion experiments could be tuned by relying on self-induced plasma gratings that can redirect laser energy directly inside NIF targets. This technique has been used on almost every NIF shot since then. "The work done by (Michel) has turned a potentially deleterious laser-plasma interaction mechanism ... into a tool for balancing the spatial distribution of power and energy into an ICF hohlraum," says the Fabre Prize award committee.

### Science on a Grand Scale

For the past decade, Livermore's Computing Grand Challenge Program has made world-class unclassified computing resources available to Laboratory scientists and engineers through a yearly competition. Winning proposals, as judged by a panel of internal and external reviewers, receive millions of hours of computing time to complete projects that push the frontiers of computational science, stimulate a scientific discipline, and enhance the value of Livermore's programs and missions. Advances in high-performance computing hardware have benefitted the program and expanded the size and scope of what can be modeled. Challenge projects span many research areas, including laser ignition experiment modeling, first-principles molecular dynamics (MD) simulations, and climate modeling. Modeling of interactions between lasers and the plasma they generate in National Ignition Facility targets enabled researchers to converge on an efficient and safe target design in time for facility completion and the start of experiments. A planetary research project to understand hydrogen's high pressure and temperature phases employed Grand Challenge resources to refine a method for enhancing first-principles MD simulation accuracy that could find much broader application. Three climate projects have used Computing Grand Challenge support to take their research to the next level in resolution and accuracy. Efforts such as these not only provide a venue for ideas to mature and develop but they also support the recruitment, retention, and skill maintenance of talented scientists.

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# The Power of High-Performance Computing for Aerospace



New simulation tools make possible cost-effective rocket engine and launch vehicle designs.

#### *Also in October/November*

- Additive manufacturing sparks a new approach to tailoring reactivity in materials.
- LLNL focuses its longstanding expertise in x-ray optics on dark matter and spent nuclear fuel.
- Strengthening biodefense efforts and human medical processes, Livermore researchers developed two microbe-detection technologies for metagenomics analysis.

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